Aggregation Control and Photochemical Behaviors in UV-Sensitive Organosilane Monolayers Bearing Naphthylmethylsulfonyl Groups

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To demonstrate a surface wettability change by a photochemical method, we designed a novel UV-sensitive organosilane adsorption monolayer formed from 1-chloro-1,1-dimethyl-2-(4-(2-naphthyl-methylsulfonyl)phenyl)ethylsilane (NP). The photochemical reaction of the NP-monolayer on a silica substrate by UV-light exposure was followed by contact angle and UV-visible absorption spectral measurements. The absorption spectrum of the NP-monolayer indicated that the photoreactive aromatic groups were in an aggregation state. To control the aggregation state, we prepared NP-monolayers on a trimethylchlorosilane (TMS) monolayer after vacuum-ultraviolet (VUV) light exposure at 172 nm. The aggregation and the surface density of the photoreactive chromophore could be successfully controlled by exposure time of the VUV-light to form bare silanol groups as NP adsorption sites. It was found that the aggregation-free NP-monolayers formed on the TMS-monolayer showed more effective contact angle changes for water than the aggregated NP-monolayer.
Key words: adsorption monolayer, organosilane, photochemistry, aggregation control, wettability

1. INTRODUCTION

The chemical modification of solid substrate surfaces by formation of self-assembled monolayers (SAMs)[1] has attracted attention in industry as well as in surface science. One approach to control dramatically and selectively surface properties such as wettability, adhesion, friction and so forth on a molecular scale is the use of photoreactive SAMs.

We and our co-workers have ever demonstrated that photoreactive monolayers are applicable to liquid crystal photoalingment,[2] light-driven liquid motion,[3] mesoporous silica alignment,[4] selective particle adsorption,[5] and selective metallization.[6] In particular, E-to-Z photoisomerization of azobenzenes is sensitive to a matrix microenvironment in which azobenzenes exist. Therefore, the photoisomerization has been used to probe a free volume and rigidity in polymer matrixes.[7] Ichimura et al. reveal that the E-to-Z photoisomerization of azobenzene moieties requires a sweep volume in organic ultrathin films of Langmuir-Blodgett monolayers and SAMs.[8,9] Nakagawa et al. suggest that the two-dimensional sweep molecular area of 0.45 nm^2 $molecule^{-1}$ is required for the photoisomerization in a monolayer state.[10] These previous works clearly imply that microenvironment control of photoactive chromophores in photoreactive SAMs is important for high-sensitive and effective photochemical reactions.

In this paper, we designed a novel UV-sensitive organosilane monolayer formed from 1-chloro-1,1-dimethyl-2-(4-(2-naphthylmethylsulfonyl)phenyl)ethyl-silane (NP). We demonstrated the wettability changes of the monolayer surfaces by UV irradiation. To achieve effective photoinduced wettability changes of the monolayer, we prepared several kinds of aggregation-controlled NP-monolayers by a photochemical means. We discussed a proceeding of the photochemical reaction in the aggregation-controlled monolayer state followed by contact angle measurement.

2. EXPERIMENT

2-1. Materials

The chemical structure of 1-chloro-1,1-dimethyl-2-(4-(2-naphthylmethylsulfonyl)-phenyl)ethylsilane[11] (NP) used in this study was indicated in the inset of Fig.1. Trimethylchlorosilane (TMS) was purchased from Aldrich and used as received. Other chemicals were of reagent grade and purchased from Kanto Kagaku, Japan.

2-2. Preparation of a NP-monolayer on a silica plate

A silica plate (10 x 30 x 1 mm) was cleaned by irradiation with vacuum-ultraviolet (VUV) light at 172 nm emitting from a Xe excimer lamp (UER20-172A, Ushio, Inc.) under a reduced pressure of 1000 Pa for 5 min. The cleaned silica plate was immersed in a toluene solution containing 1 wt% NP at 30 °C for 1 h, followed by multiple rinses with a pure toluene and methanol. A silica plate absorbing NP, as abbreviated as a NP-monolayer, was obtained by blow-drying with N_2 gas.

2-3. Preparation of NP-monolayers on a VUV-exposed TMS monolayer

A cleaned silica plate was immersed in trimethylchlorosilane (TMS) at 30 °C for 1 h, followed by multiple rinses with toluene and methanol. The silica plate modified with a TMS monolayer was exposed to VUV-light at 172 nm under an air atmosphere. The face-to-face distance between a VUV-light source and the TMS monolayer was 19.7 mm. Five kinds of VUV-exposed TMS monolayers subjected to VUV-exposure for 0, 100, 300, 600, and 900 seconds were prepared. The VUV-exposed TMS-monolayers were immersed in a 1 wt% NP toluene solution at 30 °C for 1 h. NP-monolayers on the VUV-exposed TMS-monolayers were obtained in a manner similar to preparation of the NP- monolayer on a silica plate.

2-4. Photoirradiation and measurements

The organosilane monolayers composed of NP were exposed to UV-light passing through a glass filter emitting from a 200-W Xe-Hg lamp. Two types of UV-light wavelengths of $\geq$ 254 and > 280 nm were used for photoirradiation. Light intensities at 254 and 310 nm were monitored with an optical power meter.

Photochemical reactions of NP-monolayers upon irradiation with the UV-light were followed by contact angle and UV-visible absorption spectral measurements. Sessile contact angles for water were measured using a Kyowa Kaimen Kagaku CA-X contact angle meter. UV-visible spectra were taken on a JASCO MAC-1 weak absorption spectrophotometer.

3. RESULTS AND DISCUSSION

3-1. NP-monolayer on a silica plate exposed to UV-light

Figure 1 shows the UV-visible spectra of 1-chloro-1,1-dimethyl-2-(4-(2-naphthylmethylsulfonyl)-phenyl)ethylsilane (NP) in hexane and a NP-monolayer
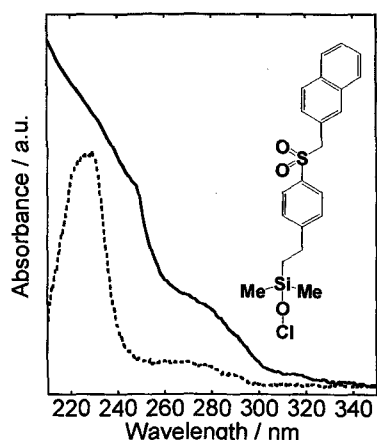

Fig. 1. UV-visible absorption spectra of NP in hexane (broken line) and an NP-monolayer on a silica plate (thick line). The inset shows the chemical structure of NP used in this study.

on a silica plate. The NP molecule in hexane exhibited two characteristic absorption bands at 225 and 270 nm with an absorption terminal of 297 nm.

The UV-visible absorption spectrum of an NP-monolayer on a silica plate was intrinsically different from that of the NP molecule in hexane. The absorption band at 225 nm observed in hexane was subjected to a blue-shift. This result indicated that the NP molecules in the NP-monolayer were in an H-aggregation state. When the NP-monolayer was irradiated with UV-light at $\geq$ 254 nm, the hydrophobic surface of the NP-monolayer changed from 89.4° to 79.2° with regard to water contact angles at a 254 nm exposure energy of 1.0 J cm^{-2}. UV-visible spectral changes of the NP-monolayer upon UV-exposure was slight in comparison with those observed for 2-naphthylmethyl phenyl sulfone as a model compound in 2-propanol (data not shown). It was anticipated that aggregation of NP molecules in a monolayer state would suppress photochemical cleavage of the naphthymethyl group to form hydrophilic benzenesulfinic acid moieties as shown in Fig.2.
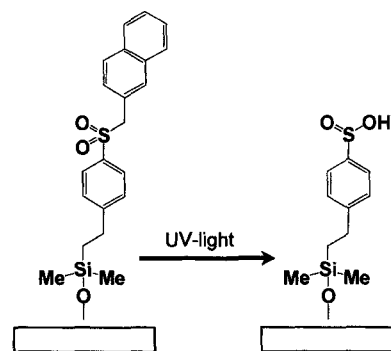

Fig. 2. Possible photochemical reaction of a NP-monolayer on a silica plate to form a hydrophilic benzenesulfinic acid moiety.

3-2. Aggregation control of NP molecules adsorbed on VUV-exposed TMS monolayers

To prepare an aggregation-free NP-monolayer on a silica plate, we would like to propose a novel method. Figure 3 indicates the new method for preparing the aggregation-free NP-monolayer. First, outermost silanol groups of a cleaned silica surface are reacted with trimethylchlorosilane. As a result, a monolayer formed from trimethylchlorosilane on a silica plate (TMS-monolayer) is obtained. Secondly, the TMS-monolayer is irradiated with VUV-light at 172 nm. Activated oxygen atoms generated by VUV-exposure oxidatively decompose methyl groups to CO_2 and H_2O species,[12] and fresh silanol groups appear again at an outermost silica surface. It is anticipated that the formation of silanol groups as adsorption sites will be controlled by VUV-exposure time, because the photodecomposition proceeded gradually and randomly. Finally, the NP molecules are adsorbed on photogenerated silanol groups in the VUV-exposed TMS monolayer. This methodology will successfully enable us to control the surface density and the aggregation state of adsorbed NP molecules.

To demonstrate the assumption to prepare aggregation-free NP-monolayers, we first investigated contact angle changes of a TMS monolayer after VUV-light exposure. Figure 4 shows the contact angles for water of a VUV-exposed TMS monolayer on a silica plate as a function of exposure time. The hydrophobic TMS-monolayer with a contact angle of 81.5 ± 2.2° turned more hydrophilic with an increase in the exposure time. The contact angle of the TMS-monolayer decreased eventually to 4.1 ± 1.6° by the VUV-exposure for 920 seconds under an air atmosphere. We chose five types of TMS-monolayers subjected to VUV-exposure time for 0, 100, 300, 600 and 900 seconds, which were abbreviated as TMS$_0$, TMS$_{100}$, TMS$_{300}$, TMS$_{600}$, and TMS$_{900}$, respectively. Thus obtained VUV-exposed TMS-monolayers were immersed in a 1 wt% NP toluene solution, to form a NP-monolayer.

The inset of Fig. 4 shows the UV-visible absorption spectra of TMS$_0$, TMS$_{100}$, TMS$_{300}$, TMS$_{600}$, and TMS$_{900}$ after immersion in the toluene solution containing a silane coupling reagent of NP. On a TMS$_0$ plate without VUV-exposure, the NP molecule was hardly adsorbed. This result suggested that an outermost
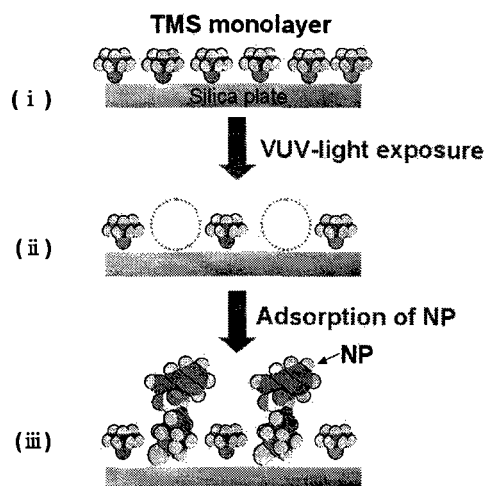
Fig. 3. Schematic illustration of preparing an aggregation-free NP-monolayer on a VUV-exposed TMS monolayer. The preparation method consists of (i) formation of a TMS monolayer, (ii) VUV-exposure to form silanol groups as adsorption sites, and (iii) adsorption of NP molecules.
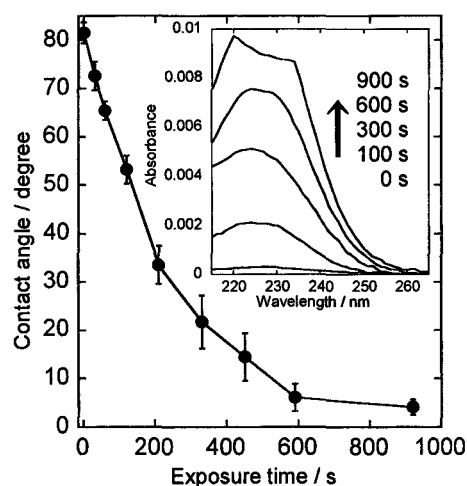

Fig. 4. Contact angle changes for water of a TMS-monolayer on a silica plate as a function of VUV-exposure time. The inset shows UV-visible absorption spectra of NP-monolayer formed on VUV-exposerd TMS monolayers of TMS_0, TMS_{100}, TMS_{300}, TMS_{600}, and TMS_{900}.

silanol groups were almost capped with trimethylsilyl groups. As a result, there was not any silanol group available for chemical adsorption of the NP molecules. As seen in the inset of Fig. 4, an absorption band at 225 nm was increased, as the VUV-exposure time to TMS-monolayer was increased. This result supported that the VUV-exposure decomposed outermost trimethylsilyl groups and formed fresh silanol groups as adsorption sites of the NP molecules. It was worthy of note that the spectral shape of the NP-monolayer similar to the NP molecule in hexane was observed for TMS_{100} and TMS_{300} plates. Because the spectral shape was slightly different on the TMS_{600} plate, partial NP molecules formed H- and J-aggregated species. Therefore, these results obviously suggested that the NP molecules on the TMS_{100} and TMS_{300} plates were in an aggregation-free state even in a monolayer state.

A molecular area per molecule on a silica plate can be estimated by UV-visible absorption spectroscopy under the assumption that a molecular absorption coefficient in a solution is not changed in a film state.[13] The estimated molecular areas per NP molecule were 2.1, 0.8 and 0.6 nm^2 for the NP-monolayer on TMS_{100}, TMS_{300} and TMS_{600}, respectively. These values were meaningfully larger than the cross-sectional molecular area of NP molecule estimated by the CPK model (0.42 nm^2). It was found that the surface density and the aggregation state of the NP molecules on a silica plate could be successfully controlled by the VUV-exposure time to the TMS-monolayer.

3-3. Photoinduced alteration of contact angles for water on density-controlled NP-monolayers

We investigated contact angle changes for water of NP-monolayers by UV-exposure at $\geq$ 254 nm. The results of the photoinduced contact angle changes were summarized in Fig. 5. The marks ●, ♦, ▲ and ■ mean the NP-monolayer on a silica plate, a VUV-exposed TMS_{100} plate, a TMS_{300} plate and a TMS_{600} plate, respectively. The aggregated NP-monolayer formed on a silica plate exhibited a contact angle change of 10.2°

(from 89.4° to 79.2°) after UV-irradiation at a 254-nm exposure energy of 1.0 J cm^{-2}. At the same exposure energy, a contact angle change by the UV-exposure was 10.5° (from 87.6° to 77.1°) for the NP-monolayer on a TMS_{600} plate. Furthermore, contact angle changes by the UV-exposure were 13.3° (from 86.6° to 73.3°) for the NP-monolayer on TMS_{300} plate and 9.3° (from 84° to 74.7°) for the NP-monolayer on TMS_{100} plate at a 254-nm exposure energy of 0.8 J cm^{-2}.

The TMS-monolayer on a silica plate showed slight changes (2.6°) in contact angle for water even after UV-exposure at a 254-nm exposure energy of 1.0 J cm^{-2}. Upon irradiation with UV-light at $\geq$ 254 nm, an absorption band at 270 nm attributable to benzene sufinic acid moieties was increased in UV-visible spectra of the NP-monolayer on the VUV-exposed TMS plates (data not shown). Taking account of the facts, the photoinduced alteration of water contact angle observed for these NP-monolayers was mainly responsible for surface photochemistry of the naphthylmethylsulfonyl group to a sufinic acid moiety as shown in Fig. 2.

Here, a noticeable point is that the photoinduced alteration of the water contact angles was almost identical, although the molecular areas estimated by UV-visible spectroscopy were significantly different. The values of area per molecule 2.1, 0.8 and 0.6 nm^2 in the NP-monolayer on a TMS_{100}, TMS_{300} and TMS_{600} plate correspond to 0.50, 1.25 and 1.70 molecules nm^{-2}. From these values, the contact angle changes of the NP-monolayer on a TMS_{600} plate should be about three folds as large as that of the NP-monolayer on a TMS_{100} plate. These results obviously implies that aggregation-free NP molecules in a monolayer state would react photochemically rather than aggregated NP molecules.

3-4. Photoinduced contact angle changes upon irradiation with UV light at > 280 nm

Since the NP molecule in hexane exhibited an absorption terminal of 297 nm, we investigated photoincuded contact angle changes of NP-monolayers
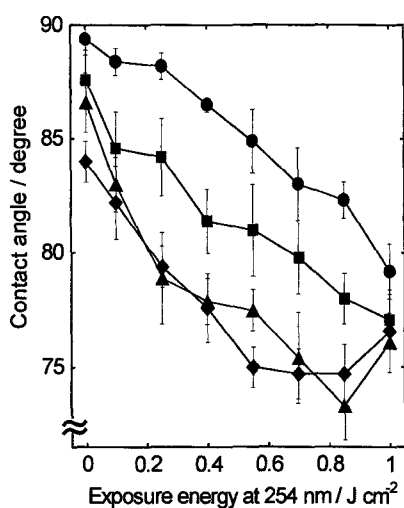
Fig. 5. Photoinduced contact-angle changes for water of NP-monolayers on a silica plate (●) and on VUV-exposed TMS$_{100}$ (♦), TMS$_{300}$ (▲) and TMS$_{600}$ (■) plates upon irradiation with UV light of ≥ 254 nm as a function of exposure energy at 254 nm.,
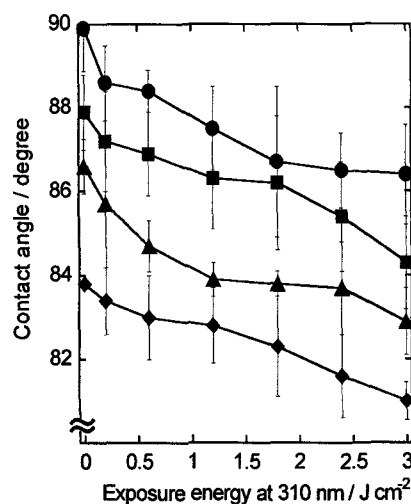
Fig. 6. Photoinduced contact-angle changes for water of NP-monolayers on a silica plate (●) and on VUV-exposed TMS$_{100}$ (♦), TMS$_{300}$ (▲) and TMS$_{600}$ (■) plates upon irradiation with UV light of > 280 nm as a function of exposure energy at 310 nm.

upon irradiation with UV-light at longer wavelengths of > 280 nm. The results were indicated in Fig. 6. The marks ●, ♦, ▲ and ■ mean a NP-monolayer on a silica plate, a TMS$_{100}$ plate, a TMS$_{300}$ plate, and a TMS$_{600}$ plate, respectively. The aggregated NP-monolayer on a silica plate showed a contact angle change of 3.5° (from 89.9° to 86.4°) at a 310-nm exposure energy of 3.0 J cm^{-2}. The contact angle change for water was 3.6° on a TMS$_{100}$ plate, 3.7° on a TMS$_{300}$ plate, and 2.8° on a TMS$_{600}$ plate. A TMS monolayer on a silica plate without VUV-exposure showed a contact angle change of 1.7° at the same exposure energy. Photochemistry hardly occurred upon irradiation with UV-light at > 280 nm, because a molar absorption coefficient in the UV region was small in the NP-monolayers. To bring about an effective photoinduced contact angle change upon UV-light at > 280 nm, we should design other chromophores.

4. CONCLUSION

We demonstrated a new method for preparing aggregation-free UV-sensitive monolayers by a photochemical technique. The UV-sensitive silane coupling reagent of 1-chloro-1,1-dimethyl-(2-(4-(2-naphthylmethylsulfonyl)phenyl)ethylsilane (NP) was adsorbed on a silica plate, to form a densely-packed aggregated monolayer. In contrast, aggregation-free NP-monolayers were successfully obtained by adsorption of the NP molecules on VUV-exposed monolayers formed from trimethylchlorosilane (TMS). As a result, we could prepare density-controlled NP monolayer in an aggregation-free state. This method for controlling a surface density of photoreactive chromophores will be useful for fabrication of well designed single-layer adsorption films on a substrate surface. Contact angle changes of the NP-monolayers upon UV light irradiation implies that aggregation-free NP molecules in a monolayer state were transformed

photochemically more than aggregated NP molecules.

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