Highly Ordered Selective Adsorption of Methyl Orange on Heterogeneous Surfaces in Aqueous Solutions

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The effect of chemical heterogeneity on the adsorption of Methyl Orange (MO) in aqueous solutions was investigated by atomic force microscopy (AFM). On hydrophilic mica, a small number of disordered islands of Methyl Orange were formed. However, after deposition of self-assembled monolayers (SAMs) of octadecyltrichlorosilane (OTS) on mica, MO molecules adsorbed extensively and selectively on the hydrophobic OTS SAMs. Most importantly, the MO molecules on hydrophobic domains were highly ordered and almost perpendicular to the OTS surface.

The selective adsorption of organic molecules on solid surfaces is not only a key technique to improve efficiency in many important heterogeneous catalytic processes but also a fundamental aspect of sensing technology and biological phenomena.[1] For instance, TiO_2 photocatalysis is a promising method for environmental remediation. However, the adsorption coefficient of many of toxic compounds on titanium dioxide is very low. Therefore, controlling the adsorption of specific molecules onto the photocatalyst surface would greatly improve the degradation efficiency.[2]

Generally, the selective adsorption on a solid surface is governed by noncovalent interaction including hydrophobic interaction, hydrogen bonding, electrostatic interaction, structure matching, and π–π stacking.[3] Selective adsorption can also occur between molecules and a functionalized surface. Self-assembled monolayers (SAMs) are often used to modify solid surfaces because of their nicely ordered structure and can tail the functional groups.

Azobenzene and its derivatives have attracted much attention due to their possible usage as molecular switches, drug carriers, optical devices, and smart materials.[4] In most cases, molecular orientation of azobenzene is an important factor for these applications. As a typical model compound, MO has been widely studied. For example, Maeda et al. reported that MO could be included in the cavity of chemisorbed cyclodextrin derivatives on Ag by structure matching.[5] Takahashi et al. reported that MO showed an edge-on configuration by adsorption on a Langmuir–Blodgett film due to electrostatic interaction.[6] Zou et al. have studied 2-D aggregate geometry of azobenzene at mica/aqueous solution interface. And electrostatic interaction could be responsible for the formation of curvature of ordered surface structures.[7]

In this work, the selective self-assembly behavior of MO on heterogeneous surfaces in aqueous solution was studied. And adsorptive selectivity and nanostructures were characterized by AFM, ATR-IR, and contact angle measurement. The possible effect of hydrophobic interactions on the adsorption is discussed.

Fresh mica was used as the hydrophilic substrate. The hydrophobic domains were prepared by partially grown OTS SAMs on mica. The substrate was immersed into a 2.0 mM solution of OTS precursor dissolved in toluene at $23.0 \pm 1.5\,^{\circ}C$ in a glove box. The deposition time was 20 s. The samples were then washed in carbon tetrachloride to remove excess reactants and dried with pure nitrogen. The partially grown OTS SAMs on mica (OTS-mica) and fresh mica were deposited in Methyl Orange solution ($3 \times 10^{-5}\,mol\,L^{-1}$) at $16\,^{\circ}C$ for 10 min under neutral conditions. Then the samples were washed with high purity water to remove excess reactants and dried in pure nitrogen. Surface nanostructure was characterized by AFM (AutoCP-R, Veeco, USA). Infrared spectra were obtained by a ATR-IR spectrometer (Nicolet 6700, USA). A sessile drop method was used for contact angle measurements at $20.0 \pm 1.5^{\circ}$ using a commercial contact angle meter (Powereach JC2000A, Shanghai, China).

On the OTS-coated mica, two main bands at 2851 and $2923\,cm^{-1}$ are clearly observed in the IR spectrum.[12] These are assigned to $\nu_s(CH_2)$ and $\nu_a(CH_2)$ modes of the OTS alkyl chains, respectively.[8] After adsorption of MO on the OTS-coated mica, the frequencies of these peaks increase to ca. 2854 and $2926\,cm^{-1}$. The intensities of the C–H stretching band increased greatly. It suggested that the MO had largely adsorbed on the OTS-coated mica. On the other hand, the water contact angle on the OTS-coated mica decreased from 72.3 ± 2.3 to $49.6 \pm 4.8^{\circ}$ after the MO adsorption. It indicated that the hydrophilicity increased. However, before and after the MO adsorption on fresh mica, no obvious change was found in the IR spectrum and contact angle.

Figure 1 shows typical AFM images (topography) and cross-sectional profile of mica after the adsorption of MO. The MO generated few clusters sparsely and randomly adsorbed on the hydrophilic mica surface. And no regular structure was found on the nanoscale. After the deposition of OTS SAMs on mica, the distribution and topography of OTS monolayers was acquired by AFM directly. AFM images showed that OTS SAMs islands formed hydrophobic domains.[12] The typical AFM images (topography and phase images) and cross-sectional profile of MO adsorption are presented in Figure 2. The MO molecules adsorbed largely on the hydrophobic OTS SAMs surface. However, on the hydrophilic domain, there were no adsorptive MO molecules. The phase images (Figure 2b) demonstrated that there were three domains with different surface properties. It indicated the MO adsorbed selectively on the hydrophobic surface. Furthermore, from the sectional analysis, the MO had multilayer structure. More importantly, the thickness of the aggregates maintained a constant value of about 1.31 ± 0.02 nm or its inte-

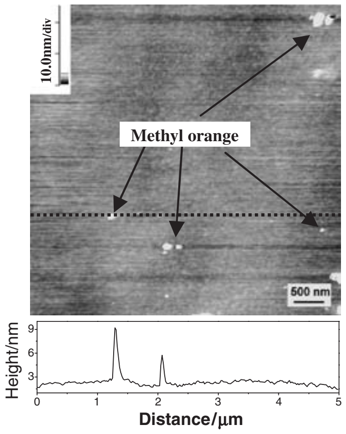
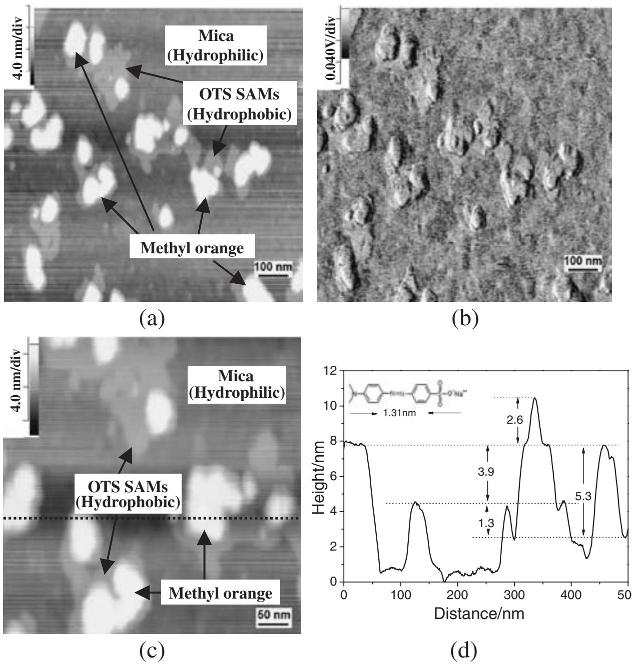


Figure 1. AFM topographic images and cross-sectional profile on mica after the adsorption of Methyl Orange (MO). Scan size is 5 × 5 μm^2.



(a) (b)

(c) (d)

Figure 2. (a) AFM topographic images and (b) corresponding phase images after the adsorption of MO on OTS-mica., Scan size is 1 × 1 μm^2. (c) AFM topographic images and (d) cross-sectional profile after the adsorption of MO on OTS-mica. Scan size is 500 × 500 nm^2.

gral multiple. The length of one MO molecule is about 1.31 nm.[6] The observed thickness of MO from AFM data was about 1–6 times this value. This suggests that the MO layers are highly ordered and approximately perpendicular to the OTS surface.

MO is an anionic azo dye with negatively charged sulfonate groups, and the azo form of MO is dominant under neutral conditions. Moreover, it is well known that mica surfaces are highly hydrophilic and negatively charged. Therefore, there is electrostatic repulsion between MO and mica, which results in little adsorption of MO on the surface. The deposition of OTS SAMs forms hydrophobic groups on the hydrophilic mica. The adsorption results demonstrated that the adsorption capacities of OTS-coated mica are much higher than those of mica. This suggests that the hydrophobic interaction between OTS and MO enhances the adsorption.[9] The hydrophobic interaction is long-range noncovalent interaction and is associated with the ordering of molecules.[10] It suggests that the hydrophobic interaction is associated with the ordering of the adsorbed MO layer which is near the methyl groups of OTS. And the first layer with ordered conformation would affect the adsorption of other MO molecules. In addition, MO can self-associate in aqueous solution.[11] Therefore, hydrophobic interaction, electrostatic interaction, and self-association of the MO could determine the molecular conformation of adsorptive MO.

In summary, the adsorption of MO on the heterogeneous surface has been studied. MO molecules adsorbed intensively and selectively on the hydrophobic domains. MO demonstrate multilayer structure and are almost perpendicular to the OTS surface. The hydrophobic interactions play an important role in formation of the ordered morphology and selective adsorption of MO on the heterogeneous surface. The result is expected to be helpful for improving degradation efficiency in photocatalysis and developing optical devices related azobenzene.

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