Atomic layer deposition of enantioselective thin film of alumina on chiral self-assembled-monolayer

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ABSTRACT

In this paper, we describe the synthesis of new chiral nanosized surfaces based on chiral self-assembled mono-layers coated with metal oxide (Al$_2$O$_3$) nanolayers. In this new type of nanosized chiral surface, the Al$_2$O$_3$ nanolayers enable the protection of the chiral self-assembled monolayers while preserving their enantioselective nature. The chiral nature of the SAMs/Al$_2$O$_3$ films was characterized by a variety of techniques, such as, quartz crystal microbalance, circular dichroism (CD) spectroscopy and chiral crystallization. The proposed methodology for the preparation of nanoscale chiral surfaces described in this article could open up opportunities in other fields of chemistry, such as chiral catalysis.

1. Introduction

In recent years, chirality at the nanoscale [1–4] and chiral surfaces [5–14] have been found to play an important role in nanotechnology, particularly chiral nanoscale surfaces and chiral nanoparticles. Generally, chiral solid surfaces can be derived from chiral bulk structures that expose chiral, enantioselective surfaces, such as quartz and other crystalline materials (typically covalent inorganic oxides) [15]. Another category of chiral solid surfaces is composed of crystalline solids produced from materials with achiral bulk structures. Such chiral surfaces are based on single crystals of metals (with bcc or hcp crystal structures) [7] that expose high Miller indices with periodic arrays of steps, terraces, and kinks. Finally, the most common method for the preparation of chiral surfaces is the adsorption of chiral molecules, typically onto metallic surfaces. The resulting surface is chiral if the adsorbed molecules retain their chirality. Although chiral surfaces based on self-assembled mono-layers (SAMs) or polymeric surfaces exhibit highly enantiospecific properties, they still suffer from many restrictions, such as low thermal stability and poor chemical and mechanical characteristics, which limit their use for chemical applications, particularly for enantioselective catalysis and chiral separation.

In our previous research we proposed an innovative type of stable nanosized chiral metal oxide surface [16]. The structure and chirality of this type of chiral surface is based on chiral self-assembled mono-layers (SAMs) coated with nanosized films of metal oxide materials (e.g. TiO$_2$). In Fig. 1 the overall design and synthetic paths for this chiral SAM/metal oxide surface are shown. The fundamental principle of design of these chiral surfaces is that the metal oxide nanolayers coating the chiral SAMs protect the chiral SAMs that would otherwise be destroyed under severe reaction conditions, while preserving their enantioselectivity [14].

Our working hypothesis, that it is feasible to design chiral surfaces based on a chiral SAM/metal oxide nanolayer hybrid system, is supported by our previous research [16,17] and that of other research groups [18,19] who showed that chirality can be templated in metal oxides to form chiral materials, such as nanoporous alumina nanofilms and meso-porous silica chiral structures. The first demonstration of the preparation of chiral metal oxide surfaces was reported by the Switzer group [20]. In a series of articles [20–22] they showed that chiral surfaces of CuO can be electrodeposited onto achiral substrates (e.g., gold) using solution-templating agents, such as tartaric acid and amino acids, to direct the chiral growth of the metal oxide surfaces.

In our previous paper [16], we described the development of this innovative type of chiral hybrid surface, based on chiral self-assembled monolayers of cysteine coated with TiO$_2$ nanolayers, and demonstrated its chiral nature using various analytical techniques, such as quartz crystal microbalance, second-harmonic generation circular dichroism (SHG-CD), circular dichroism spectroscopy, and chiral crystallization.

Generally, many inorganic metal oxides, such as silica, zeolite, alumina, zirconia, ZnO, clay, and others, can be used as supports for chiral SAMs. In this paper we extend our research and demonstrate the basic principle of this type of chiral hybrid surface for other chemical systems. We decided to use Al$_2$O$_3$ monolayers to form protective layers on the chiral SAMs, mainly because the atomic layer deposition synthesis of Al$_2$O$_3$ does not require high temperature processing that could harm the chiral SAMs. Various growth techniques can be applied to synthesize ceramic nanolayers on chiral SAMs such as vacuum-based methods including chemical vapor deposition (CVD) and metal organic CVD (MOCVD), or chemical solution methods including sol–gel, electrochemical deposition, and hydrothermal synthesis. However, in this work we utilize the atomic layer deposition (ALD) technique [23,24]
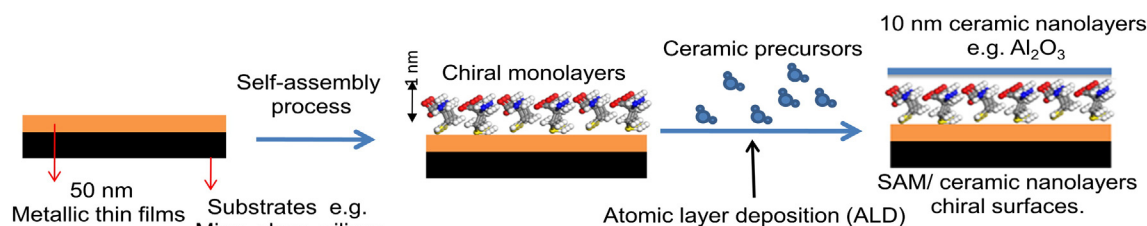
Fig. 1. Illustration of the design and the synthesis paths for the new chiral SAMs/metal oxide surfaces.

since it provides excellent thickness control and produces very dense and uniform layers.

2. Material and methods

Gold films were deposited on mica, $KAl_2(AlSi_3O_{10})(OH)_2$. Typically, a 50 nm thick layer of gold (99.995%) was sputtered on freshly cleaved mica sheets at a pressure of approximately 1×10^{-3} mbar with a deposition rate of 0.5 nm s^{-1}. Chiral SAMs were formed on the gold surfaces by immersing the gold substrates overnight in 10 mM solutions of D, L-cysteine or L-glutathione (Fig. S1) in deionized water. After removal from the solutions, the chiral SAMs surfaces were washed thoroughly with water and blown dry with nitrogen.

2.1. Atomic layer deposition (ALD)

The samples were introduced into the ALD system (Cambridge, Fiji F200). The Al_2O_3 thin films were deposited onto chiral SAMs surfaces using a $Al(CH_3)_3$ precursor and water. Ar served as both the carrier and the purging gas. Thin films of Al_2O_3 were grown on the chiral SAMs at 373 K under 1×10^{-2} Torr. The ALD cycle consisted of 0.06 s exposure to $Al(CH_3)_3$ (evaporated at 348 K), 10 s Ar purge, and a 0.06 s exposure to water. A total of 130 ALD cycles were used to obtain Al_2O_3 films with a thickness of 8.9 nm.

2.2. High-resolution transmission electron microscope (HR-TEM)

Images were taken with a 2100 JEOL microscope working at a voltage of 200 kV and were recorded on a CCD 4 × 4 k camera (Gatan). EDS chemical analysis was performed with a Thermo electron group system.

2.3. X-ray photoelectron spectroscopy analysis (XPS)

XPS analyses were performed in a Kratos AXIS-HS spectrometer, using a monochromatized $Al_{K\alpha}$ source. Survey and high resolution spectra were acquired at 75 or 150 W, respectively. All data acquisitions were performed at detection pass energies of 40–80 eV. All XPS measurements were carried out at room temperature, under vacuum conditions of $(1.0–3.0) 10^{-9}$ Torr. Spectra were acquired with a low electron flood gun for charge neutralization. The spectrometer energy scale was routinely calibrated according to the ISO TC/201 SC7 international procedure for binding energy (BE) with Au 4f 7/2 83.98 and Cu 2p 3/2 932.67. Spectra binding energy were not corrected for charging shifts. Data processing was done with VISION software (Kratos).

2.4. Quartz crystal microbalance (QCM)

Changes in the resonance frequency as a result of adsorption processes on the sensor electrode were monitored by a SRS QCM 200 sensor (Stanford Research Systems, Sunnyvale, USA) system. AT-cut quartz crystals with gold electrodes and a fundamental oscillating frequency of 5 MHz (Stanford Research Systems, Inc.) were used as sensing substrates. The sampling period and the resolution of the frequency counter

were 1 s and 0.1 Hz respectively. All the measurements were done at room temperature.

2.5. Circular dichroism (CD)

CD spectra were recorded on a Chirascan CD spectrometer (Applied Photophysics) using a bandwidth of 1 nm, from 600 to 350 nm. The step size and time were set at 1 nm and 0.5 s respectively. During the CD measurement, each surface was rotated in 90° intervals from 0° to 270°.

2.6. Enantioselective crystallization

In all crystallization experiments, analytical grade amino acids (>99.9%) were purchased from Sigma Aldrich and used as received. The experiments were conducted with supersaturated solutions of DL-threonine (7.5 g) and DL-valine (2.875 g) in deionized water (25 ml). Thereafter, the solutions were heated to 75 ºC and stirred until they were completely dissolved and left to cool to room temperature. Finally, the chiral surfaces were placed vertically in the crystallization solutions. Macrosized crystals crystallized at the chiral surfaces were detected and removed manually from the chiral surfaces; the enantiomeric excess (ee) in both crystals crystallized on the surfaces and bulk crystallization solutions were measured separately, in order to determine the amount of chiral separation. Specific light rotation was measured with a JASCO digital polarimeter (Model P-1010 $\lambda = 589$ nm, $\pm 0.05°$ accuracy) using a cylindrical quartz cell (10 mL, L = 100 mm) at room temperature by dissolving the crystals in water.

3. Results and discussion

The first step in the synthesis of this type of nanochiral surface requires the preparation of chiral SAMs. Generally, chiral SAMs can be produced by reacting gold substrates with thiols that feature chiral groups at the tail terminus. Gold films of 50 nm thickness were deposited on mica substrates using a high-vacuum sputtering technique. AFM measurements of the gold films show very smooth films with an average root–mean–square (RMS) roughness of 5 Å and typical gold grain sizes of 60 nm [16]. X-ray diffraction measurements of the gold films indicate strong orientation of the gold films along the (111) crystal plane [16].

For the chiral SAMs, we used enantiomers of cysteine and glutathione. The chiral SAMs were formed on the gold surfaces by immersing the gold substrates in 10 mM solutions of cysteine or glutathione in water overnight. The formation and structure of the chiral SAMs on the gold surfaces were verified using various techniques. X-ray photoelectron spectroscopy (XPS) of the chiral SAMs on the gold surface shows typical Au 4f (81 eV), N 1 s (398 eV), and C 1 s (282 eV) peaks. In addition, the sulfur (S 2p) peak seen at 159 eV is attributed to the S–Au bond. Finally, contact angle measurements of the bare gold (contact angle of 67°) and of the D or L-cysteine SAMs (contact angle of 18° and full spread for glutathione) indicated the formation of homogenous self-assembled monolayers on the gold surfaces.

Al_2O_3 films were grown by ALD using $Al(CH_3)_3$ as the precursor, following the process described previously [25]. Briefly, films were grown