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Effects of functional groups on the crystallization of ferric (oxyhydr)oxides

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ABSTRACT

Effects of four functional groups on the crystallization of ferric (oxyhydr)oxides were investigated in this paper. Hydroxyl (−OH), amino (−NH_2), methyl (−CH_3) and mercapto (−SH) were used to modify the surfaces. Substrates were immersed into the biomineral solution for 40 h. The biominerals crystallized on the surfaces have been examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Atomic force microscope (AFM) was used to observe the morphology of the functional group surfaces, which turned out to be of the same density. Growth of orthorhombic FeOOH was identified on all four functional group surfaces, hematite was also detected on the −NH_2 surface. While on the controlled surface of Au, no deposition of iron compounds was found. These results demonstrated different crystallization process of ferric (oxyhydr)oxides induced by functional groups.

1. Introduction

Biomineralization of iron compounds is an important part of the nature which had been broadly investigated and gained a lot of process [1–6]. The iron oxides represent an important basic material due to their large occurrence on earth. Iron mineral has a great effect on the environment. The oxidation and dissolution processes of iron mineral existed widely in soil, sediment and water, have a direct effect on the decomposition of organic matter, release of trace elements, physical and chemical properties of soils. It has been well known that iron oxides are extensively used in the production of pigments, gas sensor, catalysis and magnetic storage devices [7–9]. Studies of iron compounds therefore had be involved in the researches for many years.

Effects of different factors on the crystallization of biominerals had been regarded to be an important issue for an extended period. Previous works involved the investigation into the influence of anions (F^-, Cl^-, NO_3^- and Br^-) [10] and polymers [11]. It has been found that the functional groups which compose the amino acids play a significant influence in the dimensional structure and function of proteins [12]. The functional groups play an important role in the growth of apatite and calcium carbonate, so it would be meaningful to note that the groups will also be included in ferric (oxyhydr)oxide formation. In this study, the usual functional groups of −OH, −NH_2, −CH_3 and −SH were used to modify the surfaces [13–17]. Different effects are presented in this paper according to the results. With the gradually focus on iron biomineralization, our study will make much sense to the investigation into effects of functional groups on iron oxides and oxyhydroxides.

2. Experiments

2.1. Preparation of Au substrates

An electron beam evaporator was taken on to prepare Au substrates by deposition of gold onto the monocrystalline silicon wafers. The prepared wafers were cut into approximately 5×5 mm^2 square coupons. Then the coupons were washed with triple-distilled water and absolute alcohol in sequence. A solution with a 7:3 volume mixture of concentrated sulfuric acid and 30% aqueous hydrogen peroxide was prepared. Wafers were put in the solution with the gold face upside. After 15 min, the substrates were rinsed thoroughly with triple-distilled water and ultrasonic cleaner (Scientz SB-120DTN, Ningbo Scientz Biotechnology Co., Ltd.) to produce clean surfaces.

2.2. Preparation of self-assembled monolayers (SAMs)

The substrates were immersed in a 1 mM solution of different alkanethiols with ethanol [18] for at least 24 h. Then the modified surfaces terminated with −OH, −NH_2, −CH_3 and −SH were washed thoroughly with triple-distilled water. Water contact angle measurement [19] was performed to confirm the presence of the desired functional end group on the surfaces of wafers.

2.3. Biomimetic crystallization

A $FeCl_3$–HCl solution was prepared by mixing a ferric chloride hexahydrate and chlorhydric acid solution in a container, the concentrations

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of $FeCl_3$ and HCl were fixed at 1 mM. The substrates were placed upside-down and immersed in the prepared solution for 40 h at 25 °C, the container was sealed during this process. Wafers were taken out from the solution at the scheduled time, and dried with nitrogen and stored sealed at −4 °C before characterization.

2.4. Sample characterization

The crystalline status on the five surfaces was investigated with an X-ray diffractometer (D/max 2500, Rigaku, Japan) immediately after taken out from the solution. CuKα1 (λ = 0.1541 nm) radiation was taken for excitation. The 2θ ranged from 25° to 75° and XRD profile was recorded in step-scan intervals of 0.02° at a scanning speed of 6.0°/min at 40 kV and 200 mA. SEM and EDS were used to characterize the biominerals. SEM was performed by S-4500 (Hitachi, Japan) with an accelerating voltage of 15 kV. Topographies and roughness of functional group surfaces were examined by an AFM machine (MFP-3D-S, Asylum Research, USA). Olympus AC160TS probe with Si_3N_4 cantilevers were used to acquire the images in open mode.

3. Results and discussion

3.1. Wettability of the surfaces by water contact angle measurements

The water contact angles of five surfaces were examined (shown in Fig. 1), water contact angle system OCA20 (Dataphysics, Germany) was performed in quintuplicate. These values obtained were in accordance with previously published data [20,21]. The results indicated that alkanethiol molecules constitute different functional groups that were well self-assembled on the surfaces.

3.2. AFM topography

From the AFM topography images of different functional group surfaces, the alkanethiols are found to be equably distributed on the Au surfaces, so only −OH was chosen as an example (shown in Fig. 2). This image identified the same surface density of functional groups terminated on the Au wafers. The modification surface patterns exhibited an average functional head intervals of 0.5 nm and the well-known ($\sqrt{3}\times\sqrt{3}$) R30° structure [22].

3.3. XRD patterns

The XRD patterns of the particles at various surfaces immersed in the solution for 40 h were presented in Fig. 3. The obvious peaks at 2θ = 28.400° which reflected crystallization of orthorhombic FeOOH (referenced to JPDS card no. 18-0639) were shown on all four functional surfaces. It is worthy to mention that the height of those peaks is really differed as can be observed from this image. On the −OH surface, the peak is the highest thus follows −SH and $-CH_3$, the lowest peak is on the $-NH_2$ surface. According to the JPDF card, this peak is the third strong peak of orthorhombic FeOOH, and it presents a preferred orientation of

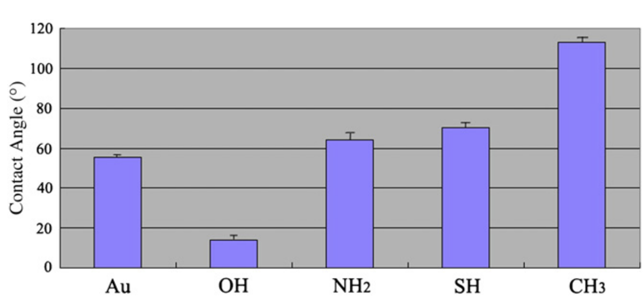

Fig. 1. Contact angle measurements using water as solvent. Results are means ± SD 5 independent experiments.

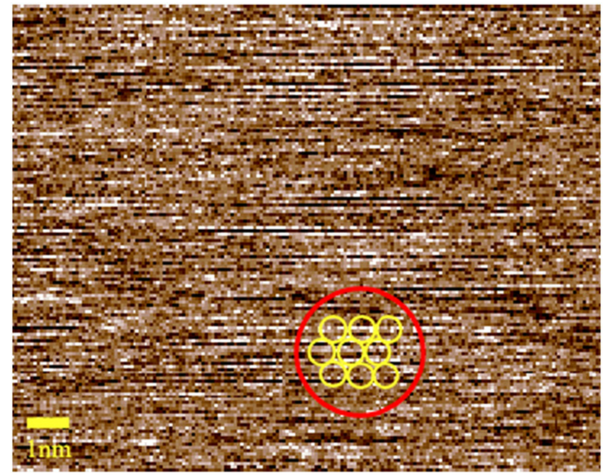

Fig. 2. AFM topography image of −OH terminated on Au (111) surface, pattern of functional groups is shown with red circles.

(130). Meanwhile, the last visible peak on the $-NH_3$ functional surface at 49.500° was consistent with the (024) reflection of α-Fe_2O_3 (closest match JPDS card no. 33-0664). Notable peaks of the (111) reflection of Au at 2θ = 38.187° (JPDS card no. 65-2870) were detected on all the five surfaces with or without modification.

3.4. Features of minerals by SEM

The morphologies of ferric (oxyhydr)oxides formed on different surfaces were observed by SEM and the magnifications of the morphology of particles were displayed in the right-bottom corner (Fig. 4A–E). On four functional group surfaces, small piles of micro-sized depositions can be seen. The average particle sizes range from 0.1 to 1 μm. Particles are disorderly distributed on the −OH surface (Fig. 4B), the enlarged picture demonstrated a curved flake morphology of orthorhombic FeOOH. A much smaller size of particles was observed on the $-NH_2$ surface where the particles displayed a small dot structure (Fig. 4C). Similar uniformly dispersed morphologies of particles were viewed on the $-CH_3$ and −SH surface (Fig. 4D, E). Meanwhile, on the surface of Au, there was hardly any amount of iron compounds (Fig. 4A). This result is well corresponded with the outcome of XRD in Fig. 3, indicated that there is no signal of iron compounds on Au surface. From those pictures, we concluded that the functional groups favor the growth of iron compounds, the surfaces have different effects on the biomineral of iron compounds.

EDS analysis corresponding to the minerals produced on the four functional groups was also put out, and the ratios of O/Fe atom of the minerals on the four surfaces turned out to be the same. So we

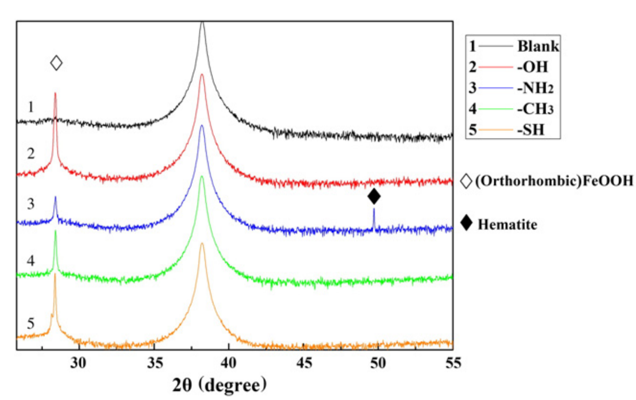

Fig. 3. XRD patterns of particles at various surfaces immersed for 40 h.