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Adsorption of TiO_2 Nanoparticles Imprinted with D-Glucose on a Gold Surface

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Adsorption of TiO_2 Nanoparticles Imprinted with D-Glucose on a Gold Surface

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A composite film of D(+)-glucose and titanium *n*-butoxide was prepared on a gold-coated quartz crystal microbalance (QCM) electrode by the surface sol-gel process. The formation of ultrathin multilayers was confirmed by frequency decrement in QCM measurements. The resulting film showed selective binding of D(+)-glucose after template removal, and its surface was densely covered with TiO_2 nanoparticles of 10-20 nm diameter.

Keywords molecular imprinting; surface sol-gel process; inorganic thin film; titanium *n*-butoxide; TiO_2 nanoparticle; D(+)-glucose

INTRODUCTION

Nanofabrication of inorganic thin films has become an important target of current materials research. Recently, we have developed a novel method to prepare ultrathin layers of metal alkoxide gels by sequential chemisorption and activation.[1,2] This surface sol-gel process can be used to design individual metal oxide layers with molecular precision, and has been widely employed for fabrication of composite layers of inorganic and organic components.[3] In addition, we also found that

organic carboxylic acids or N-protected amino acids can be molecularly imprinted in TiO_2 gel layers as matrix.[4,5] The imprinted gel films displayed structural selectivity for the template molecules. In this study, we report molecular imprinting of D(+)-glucose on a TiO_2 gel ultrathin film and its surface structure.

EXPERIMENTAL

D(+)-glucose (D(+)-Glc) was used as a template. First, $Ti(O^nBu)_4$ (1.0 mmol) and D(+)-Glc (0.05 mmol) were mixed in 5 ml of a 1:1 (v/v) toluene-ethanol mixture, and vigorously stirred at room temperature until D(+)-Glc was dissolved completely. After the solution became transparent, the stirring was continued for more than 12 h. This stock solution was diluted by 5 times with toluene and used as a dipping solution. A gold-coated quartz crystal microbalance (QCM) resonator (9 MHz, USI system, Fukuoka) modified with mercaptoethanol was immersed in the dipping solution for 5 min at 30 ℃, and rinsed in toluene. The QCM electrode was then immersed in water-saturated toluene for 3 min to hydrolyze the chemisorbed alkoxide, dried by flushing with N_2 gas, and frequency shift was measured.

RESULTS AND DISCUSSION

Figure 1 displays the QCM frequency decreases ($-\Delta F$) due to adsorbed mass in each cycle. Uniform adsorption was observed up to at least 10 cycles with average frequency shift of 90 ± 19 Hz for one cycle. The linear frequency decrements indicate regular growth of TiO_2-D(+)-Glc composite gel on the electrode. In order to remove the template molecule, the gel film was treated with 1 wt% aqueous ammonia for 20 min, washed in deionized water and in dilute hydrochloric acid (pH 4), and followed by washing in water. Frequency change was measured over silica gel after drying with N_2 gas. The frequency increase upon

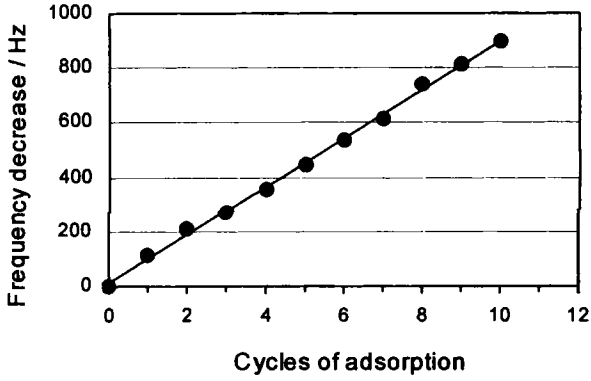
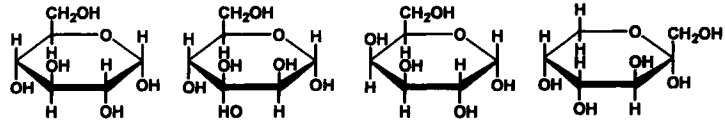


Figure 1. QCM frequency shifts in the adsorption of a mixture of $Ti(O^nBu)_4$ and D(+)-Glc. Total frequency shift was 896 Hz.

template removal was 152 Hz, corresponding to 17% of total adsorbed mass.

Subsequently, in situ QCM measurements[4,5] were carried out for rebinding experiments of the template and other monosaccharides such as mannose, galactose, and fructose (Scheme 1). The imprinted film was vertically dipped in 2 ml of 20 mM guest solution in water. Among the monosaccharides, the template, D(+)-Glc, showed the largest binding of 106 Hz, and other monosaccharides did not exceed 50 Hz. In our system with 9 MHz resonator, frequency decrease of 1Hz corresponds to mass increase of about 0.9 ng. The separation factors (α = $M_{template}/M_{guest}$, mol/mol) of three monosaccharides except for D(+)-Glc were 3.5-4.4.

Scheme 1



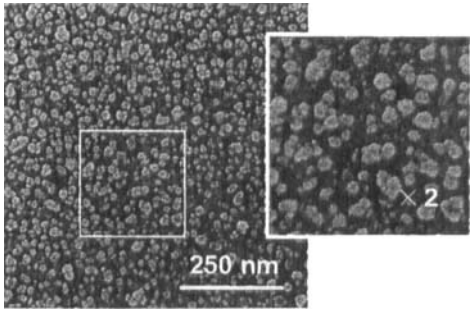


Figure 2. Scanning electron micrograph of a TiO_2-gel film imprinted with D(+)-glucose on a gold-coated QCM resonator.

After template removal, the surface of the imprinted TiO_2 gel film was observed by scanning electron microscopy (SEM, Hitachi S-900). As shown in Figure 2, the surface was densely covered with TiO_2 nanoparticles of 10-20 nm diameter. The detailed analysis on the formation of TiO_2 nanoparticle is being carried out at present.

CONCLUSION

TiO_2 nanoparticles imprinted with glucose were capable of recognition for related sugar derivatives. This method can be extended to the preparation of other imprinted nanoparticles.

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