

Imprinting of Coordination Geometry in Ultrathin Films via the Surface Sol–Gel Process

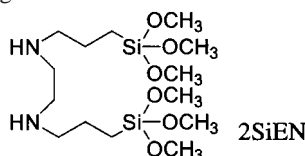
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Imprinting of Cu^{2+} and Zn^{2+} ions was performed in ultrathin TiO_2 films by the surface sol–gel process. The imprinted films showed stable and selective binding to template ions over the control metal ion. The selectivity is attributed to the immobilized geometry of ethylenediamine ligand.

Molecular imprinting aims to immobilize shapes and functionalities of templates in solid matrices via covalent¹ and non-covalent² interactions. This strategy has been applied to a wide range of organic templates, such as pharmaceuticals, pesticides, peptides, nucleotide bases, steroids, and sugars. Metal ions are similarly important targets of imprinting, although they received much less attention.^{3,4} The conventional imprinting technique is associated with some drawbacks, such as low binding efficiency, slow binding process and difficult fabrication, as the imprinted sites are embedded in bulk polymer matrices, and ready access of guest molecules to imprinted binding sites is often suppressed. These drawbacks are relieved at least partially by the use of surfaces, e.g., metal-ion imprinting on the surface of polymer particles⁵ and on the inner wall of microporous silica.⁶ We recently developed a new imprinting technique for organic molecules in ultrathin TiO_2 -gel matrices.⁷ In the present study, this technique is applied to imprinting of metal ions by incorporation of a carefully selected ligand.



We selected Cu^{2+} and Zn^{2+} ions as template because they have the same charges and almost the same ionic radii, and represent one of the most stringent challenges in the imprinting concept. Bis[3-(trimethoxysilyl)propyl]ethylenediamine (2SiEN) was chosen as the ligand. It is an ethylenediamine (en) derivative, two nitrogen atoms of which are linked to two silicon methoxide groups through trimethylene chains. When $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 2SiEN were mixed in the 1:2 molar ratio in toluene/ethanol (1/1, v/v), a $[\text{Cu}(\text{2SiEN})_2]^{2+}$ complex was formed. The complex formation is supported by its visible absorption in methanol, λ_{max} 594 nm, ϵ_{max} 109 $\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ that is close to that of $[\text{Cu}(\text{en})_2]^{2+}$, λ_{max} 549 nm, ϵ_{max} 72.1 $\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$, and is far from that of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, λ_{max} 792 nm, ϵ_{max} 30.5 $\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$. The red shift of the absorption peak from 549 nm to 594 nm is probably caused by the bulky substitution, which results in a somewhat larger distance between metal ion and ligand.⁸ The surface sol–gel process was conducted by dipping mercaptoethanol-modified gold-coated QCM electrodes in precursor solutions⁹ for 10 min, followed by rinsing in toluene, drying with nitrogen gas, and hydrolysis in air (Figure 1a). The frequency was recorded after its change probably due to progress of the hydrolysis of surface

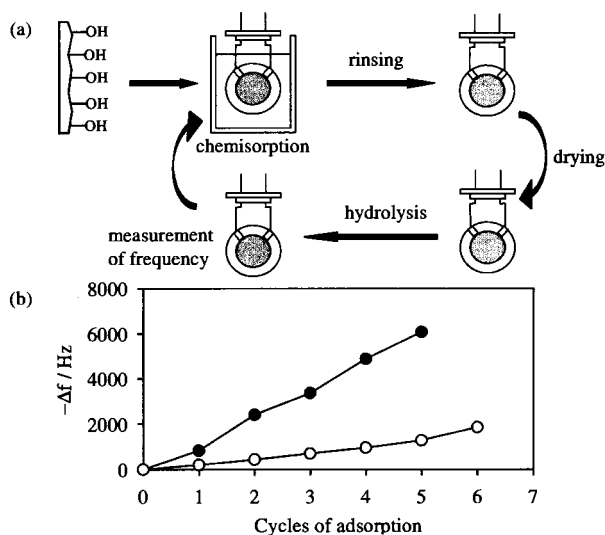


Figure 1. (a) Schematic procedure of film assembly; (b) QCM frequency shifts ($-\Delta f$) during the assembly of Cu^{2+} imprinted film (●): $\text{Cu}^{2+}/10 \text{ mM}$, $2\text{SiEN}/20 \text{ mM}$, $\text{Ti}(\text{O}-n\text{Bu})_4/100 \text{ mM}$, $\text{H}_2\text{O}/100 \text{ mM}$, 30°C , and Zn^{2+} imprinted film (○): $\text{Zn}^{2+}/10 \text{ mM}$, $2\text{SiEN}/20 \text{ mM}$, $\text{Ti}(\text{O}-n\text{Bu})_4/100 \text{ mM}$, r.t., solvent of dipping solution: toluene/ethanol (1/1, v/v), rinsing solvent: toluene.

alkoxide groups became insignificant. Chemisorption, rinsing, drying and hydrolysis constitute one cycle of the adsorption process. Figure 1b shows frequency decreases ($-\Delta f$) with adsorption cycles when Cu^{2+} or Zn^{2+} was used as the template. The linear relationship indicates regular growth of ultrathin layers. Film thickness can be estimated from frequency shift.¹⁰ It is 98 nm for the Cu^{2+} imprinted film, and 30 nm for the Zn^{2+} imprinted film. Partial hydrolysis of the alkoxide mixture appeared to result in a larger film thickness in the case of Cu^{2+} imprinting. Scanning electron micrographs indicate that these ultrathin films have flat, uniform surface morphologies.

The metal ions were removed by acidifying the amine groups with aqueous HCl (pH 4), followed by neutralization with aqueous NaOH (pH 10). The QCM frequency increased after removing metal ions. This frequency shift is related to the removed mass of template and denoted as $\Delta f_{\text{removed}}$. It increases linearly with film thickness, indicating the incorporation of template is proportional to film thickness. The total frequency shift during film assembly is related to the film mass and denoted as Δf_{film} . The ratio, $\Delta f_{\text{removed}}/\Delta f_{\text{film}}$ is plotted against film thickness in Figure 2. The ratio, $m_{\text{template}}/m_{\text{film}}$ could be estimated from the composition of precursor solution (Figure 2, solid line), where m_{template} and m_{film} are mass of the incorporated template and film mass, respectively.¹¹ The $\Delta f_{\text{removed}}/\Delta f_{\text{film}}$ plots agree with the $m_{\text{template}}/m_{\text{film}}$ values at all these film thicknesses, implying that the template has been completely removed, irrespective of film thickness.

The effect of imprinting was studied by rebinding experiments. Films were immersed for 10 min in 10 mM metal-ion nitrate in ethanol. The rebound masses were less than 1/3 of the

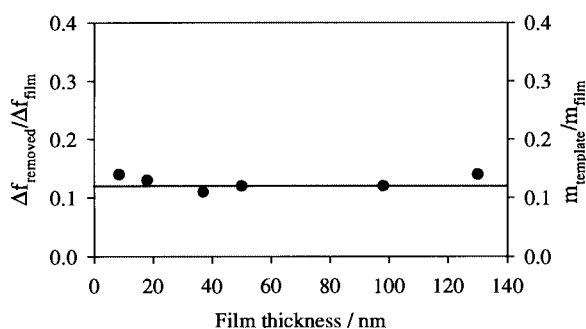


Figure 2. Dependence of $\Delta f_{\text{removed}}/\Delta f_{\text{film}}$ (●) and $m_{\text{template}}/m_{\text{film}}$ (—) on film thickness.

total template used, since the binding sites in the lower layers acted much less effectively for rebinding of metal ions. The Cu^{2+} imprinted film (Figure 3a) demonstrates greater binding to Cu^{2+} than to Zn^{2+} . The selectivity calculated from the first two bindings is $m_{1-\text{Cu}^{2+}}/m_{2-\text{Zn}^{2+}} = 10$. The Zn^{2+} imprinted film (Figure 3b), on the other hand, demonstrates greater binding to Zn^{2+} than to Cu^{2+} . The selectivity is much lower, the average $m_{\text{Zn}^{2+}}/m_{\text{Cu}^{2+}}$ being 1.3. Both of the films exhibit fairly stable binding capacity after repeated removal-rebinding cycles, though the Cu^{2+} imprinted film appears more stable. After 4 cycles, 93% of the binding capacity remains for the Cu^{2+} imprinted film ($m_{5-\text{Cu}^{2+}}/m_{1-\text{Cu}^{2+}} = 93\%$), 71% remains for the Zn^{2+} imprinted film ($m_{5-\text{Zn}^{2+}}/m_{1-\text{Zn}^{2+}} = 71\%$).

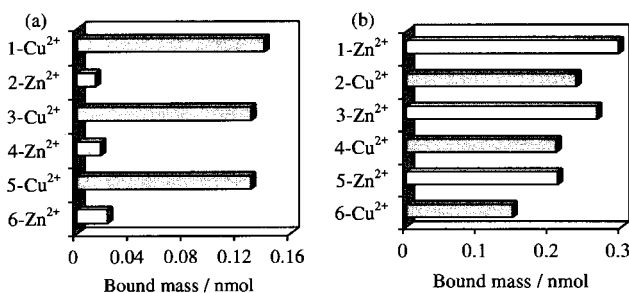


Figure 3. Repeated binding of Cu^{2+} and Zn^{2+} onto Cu^{2+} (a) and Zn^{2+} (b) imprinted ultrathin films. (a) and (b) are not comparable in the amount of rebound metal ions.

The above results are supported by X-ray photoelectron spectroscopy (XPS). In the XPS spectrum of a Cu^{2+} imprinted film, peaks were observed at 104.8 eV (Si 2p) and 403.1 eV (N 1s), 936.6 eV (Cu 2p₃) and 410.4 eV (N–O), showing that the ligand and $\text{Cu}^{2+}/\text{NO}_3^-$ have been incorporated into the TiO_2 -gel film (462.0 eV/Ti 2p₃) during the assembly. Competitive binding was tested by immersing the Cu^{2+} imprinted film in a mixture of $\text{Cu}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ (5 mM each) in ethanol. The atomic ratio of bound Cu^{2+} to Zn^{2+} , as determined by XPS, was 8.2, in close agreement with the selectivity value (10) obtained from QCM studies.

Cu^{2+} and Zn^{2+} ions assume square planar and tetrahedral configurations respectively as ethylenediamine chelates (Figures 4a and 4b). The observed binding selectivity may arise from the configurational difference. Although the stability constant of $[\text{Cu}(\text{en})_2]^{2+}$ ($\beta_2 = 19.6$) is much larger than that of $[\text{Zn}(\text{en})_2]^{2+}$ ($\beta_2 = 10.62$), the Zn^{2+} imprinted film shows stronger binding towards Zn^{2+} . During the surface sol-gel process, different configurations of the diamine ligand are apparently fixed in matrices, depending

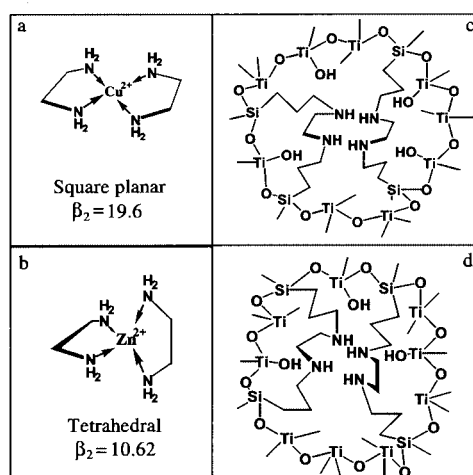


Figure 4. Configurations of $[\text{Cu}(\text{en})_2]^{2+}$ (a) and $[\text{Zn}(\text{en})_2]^{2+}$ (b), and schematic representations of the Cu^{2+} (c) and Zn^{2+} (d) imprinted sites (after template removal).

on the template metal ion. Removal of the template leaves behind nanocavities in which amine ligands are immobilized in the same configuration as the template/ligand complex. Therefore, the imprinted film can provide selective rebinding to its template rather than to the control (Figures 4c and 4d). The double linkages of the ethylenediamine group to the TiO_2 -gel network help to fix these configurations within ultrathin films, providing stable binding capacity. Other interactions, such as hydrogen bonding, van der Waals interactions might also help to fix the configurations, contributing to the selectivity and stability of binding capacity.

In the present work, the surface sol-gel technique is shown to provide a useful tool to imprint coordination geometry within ultrathin matrices. Additional advantage is that the imprinted films may be prepared on flat surfaces or on curved surfaces of microparticles. We demonstrated previously that metal oxide ultrathin films, by themselves, can produce imprinted cavities for organic molecules. It is clear that incorporation of the chelating function made it possible to create imprinted cavities for metal ions.

References and Notes

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- Cu^{2+} imprinting: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 2SiEN (62% in methanol) were mixed in ethanol, followed by addition of $\text{Ti}(\text{O}-n\text{Bu})_4$. Zn^{2+} imprinting: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ti}(\text{O}-n\text{Bu})_4$ were mixed in ethanol, followed by addition of the 2SiEN solution.
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- $m_{\text{template}}/m_{\text{film}} = \frac{C_{\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}} \times M_{\text{Cu}(\text{NO}_3)_2} / [C_{\text{Ti}(\text{O}-n\text{Bu})_4} \times M_{\text{TiO}_2} + C_{2\text{SiEN}} \times (M_{2\text{SiEN}-6\text{CH}_3}) + C_{\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}} \times M_{\text{Cu}(\text{NO}_3)_2}]}{C}$; C: concentration, M: formula weight.