Dopamine recognition in templated silicate films

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Dopamine templated nanoporous silica gel films prepared *via* the hydrolysis and cocondensation of tetramethoxysilane with phenyltrimethoxysilane show an enhanced affinity for dopamine and its related structures relative to non-templated films.

Considerable attention has recently been given to the design and development of new materials with improved molecular recognition capabilities.[1] Materials with tailor-made porosity, morphology, and chemical functionality are particularly important in the development of highly selective chemical sensors, stationary phases for HPLC, binding assays, polymeric membranes, and catalytic supports. One of the most promising technologies for the creation of recognition sites within a host structure involves molecular templating.[2,3] In this approach, a polymeric network is assembled around a suitable template molecule. Upon removal of the template, microcavities with a distinct pore size, shape and/or chemical functionality remain in the host.

Sol–gel technology provides a valuable approach for the creation of nanostructured silicate materials through the hydrolysis and condensation of silicon alkoxides.[4] The inherent processing flexibility enables thin films to be readily fabricated whereas the mild polymerization conditions enable specific reagents to be readily introduced within the highly cross-linked, porous host structure without the problems of thermal or chemical decomposition.[5] In previous work it has been demonstrated that nanostructured silica with enhanced porosity can be prepared *via* template-based sol polymerization.[3] In one method, surfactant molecules are used as templates to prepare periodic mesoporous silicate materials.[3,6] In the second method, molecular sized voids are created in a silicate matrix *via* the pyrolysis of the organic functional groups[3,7] covalently bound to the silicate framework.[8] While the pore size and connectivity of the host structure can be designed at the molecular level *via* careful control of the template concentration and sol–gel process conditions,[3] improvements in chemical selectivity need to be made.

In this report, we describe a unique template based method for the fabrication of thin porous chemically selective films, that can be used to fabricate materials with improved properties. This procedure involves the blending of organosilicon precursors with the inorganic reagents to produce a composite material[8] that shows an increased affinity for a specific class of molecules once the template has been extracted from the gel. The inorganic silicon precursor acts as the cross-linking agent whereas the organosilicon precursor introduces a specific functionality in the matrix which improves chemical specificity *via* an increase in porosity, polarity and/or intermolecular interactions. The feasibility of this approach is demonstrated in this work *via* the development of a material that shows an affinity toward dopamine and its related structures. The catechol amines were selected because of the important role they play in neurotransmission and the necessity of developing methodologies that allow their differentiation in the presence of numerous interferents including ascorbic acid (AA).[9]

In these experiments, a sol stock solution was prepared by combining tetramethoxysilane (TMOS), phenyltrimethoxysilane (PTMOS), ethoxy ethanol (EE), water and 0.1 M hydrochloric acid. PTMOS was selected as the functionalized monomer because it is a trifunctional silane containing a bulky, aromatic constituent whereas EE was utilized as the solvent owing to its both polar and non-polar solvating properties. After stirring for 1 h, dopamine was added to the sol followed by the addition of potassium hydroxide to raise the pH of the sol to *ca.* 7. The molar ratio of monomers to template was 1 : 0.1 : 0.04 (TMOS : PTMOS : DA). After 30 min, a 50 μl aliquot of the sol was cast on a polished glassy carbon electrode (5 mm diameter) using an in-house built rotator (*ca.* 7000 rpm, 60 s) and the resulting films allowed to dry for 2 days in a desiccator at ambient temperature. The average film thickness as measured *via* surface profilometry was *ca.* 450 nm. The template (*e.g.*, dopamine) was leached out of the matrix by placing the film in pH 7 phosphate buffer for 2 h. Under these conditions, approximately 90% of the dopamine was leached out of the film as evident from a cyclic voltammogram (CV) of gel-encapsulated dopamine acquired before and after leaching. In control experiments, non-templated films were prepared in a similar manner with the exception that dopamine was not added to the sol.

To characterize the affinity of the templated and non-templated films for dopamine and its structurally related compounds, cyclic voltammetry was used. Fig. 1(*a*) shows a CV at a non-templated film prepared from an undoped PTMOS–TMOS sol in a solution of 0.1 mM dopamine. The lack of significant faradaic current indicates the film is compact and dopamine is unable to reach the underlying electrode surface. In distinct contrast, the films prepared from a doped PTMOS–TMOS sol show a distinguishable affinity for dopamine as evidenced from the quasi-reversible voltammogram obtained at the templated film, Fig. 1(*b*). The peak current for the oxidation of dopamine achieves a constant value within 3–4 min indicative of the relatively fast response of the templated films toward dopamine. The response of the templated film toward dopamine is *ca.* 70% of that observed for an identical solution concentration at a bare glassy carbon electrode.

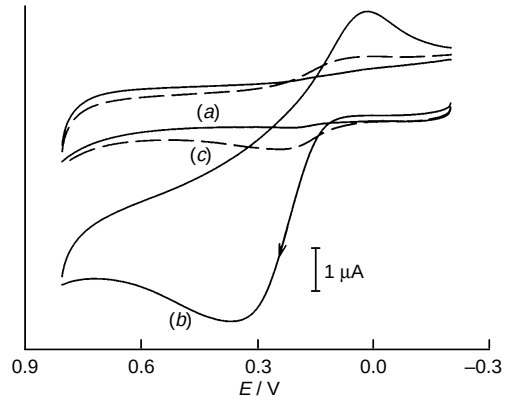

Fig. 1 Cyclic voltammograms (CVs) of 0.1 mM dopamine at (*a*) a non-templated PTMOS–TMOS film, (*b*) a templated PTMOS–TMOS film and (*c*) a templated film prepared from TMOS. The CVs were acquired after the silicate films had been in solution for 4–5 min. Solution conditions: 0.1 M, pH 7.0 phosphate buffer. Scan rate = 100 mV s^{-1}. Electrode potentials are *vs.* Ag/AgCl (1.0 M KCl).

To establish the importance of the phenyl functionality in the recognition properties of the material, templated films were prepared only from TMOS. The CV response of the templated TMOS film toward dopamine is slight as shown in Fig. 1(*c*), but significantly less than that observed at the templated PTMOS–TMOS silicate film. These results attest to the importance of the organosilicon precursor in enhancing the response of the film toward dopamine.

The dopamine templated PTMOS–TMOS films were also exposed to solutions of structurally related or biologically significant compounds including epinephrine, norepinephrine and ascorbic acid. These results showed that the templated films were not selective solely for dopamine but have an affinity for other catechol amines as well. This is expected since the host matrix is sufficiently porous and lacks specific binding sites as commonly observed for molecularly imprinted polymers.[2] The templated films, however, are able to discriminate against ascorbic acid as shown in Fig. 2. The lack of a noticeable voltammetric signal at the templated PTMOS–TMOS film and the non-templated PTMOS–TMOS film indicates that these materials have little affinity for ascorbic acid. The basis of this discrimination is likely due to electrostatics as the silicate matrix (pK_a of the silanol groups[10] is *ca*. 2) and ascorbic acid are both negatively charged at neutral pH. Alternatively, polarity may also be another factor as ascorbic acid is a relatively polar molecule whereas the phenyl-modified silicate films are more nonpolar.

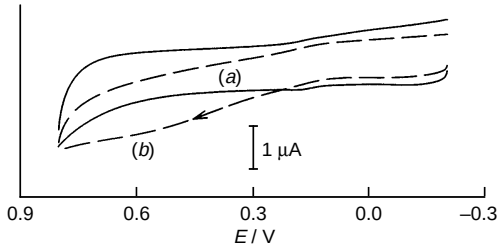

Fig. 2 Cyclic voltammograms of 0.1 mM ascorbic acid at (*a*) a nontemplated PTMOS–TMOS film and (*b*) a templated PTMOS–TMOS film. The CVs were acquired after the silicate films had been in solution for 4–5 min. Solution conditions: 0.1 M, pH 7.0 phosphate buffer. Scan rate = 100 mV s^{-1}. Electrode potentials are *vs.* Ag/AgCl (1.0 M KCl).

In summary, this study has demonstrated the feasibility of utilizing aqueous based inorganic polymerization techniques to fabricate nanoporous templated films with short response times that exhibit chemical selectivity. It is anticipated that this work will lead to promising developments in the design of improved molecular recognition materials.

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Notes and References

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1 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304.
2 D. Kriz, O. Ramstrom and K. Mosbach, *Anal. Chem. A*, 1997, 345.
3 N. K. Raman, M. T. Anderson and C. J. Brinker, *Chem. Mater.*, 1996, **8**, 1682.
4 J. Brinker and G. Scherer, *Sol–Gel Science*, Academic Press, New York, 1989.
5 D. Avnir, *Acc. Chem. Res.*, 1995, **28**, 328.
6 H. Yang, N. Coombs, I. Sokolov and G. Ozin, *Nature*, 1996, **381**, 589; H. Yang, N. Coombs and G. Ozin, *Nature*, 1997, **386**, 692.
7 N. K. Raman and C. J. Brinker, *J. Membr. Sci.*, 1995, **105**, 273.
8 J. Wen and G. L. Wilkes, *Chem. Mater.*, 1996, **8**, 1667.
9 R. M. Wightman, L. J. May and A. C. Michael, *Anal. Chem. A*, 1988, **60**, 769.
10 R. K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979.

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