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pH- and Ionic Strength-Controlled Cation Permselectivity in Amine-Modified Nanoporous Opal Films

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The influence of pH and ionic strength on permselective transport in nanoporous opal films prepared from 440 nm silica spheres was investigated by cyclic voltammetry in aqueous and acetonitrile solutions. Three-layer opal films were deposited from a 1.5 wt % colloidal solution of silica spheres onto 25- μ m-diameter Pt microdisk electrodes shrouded in glass. The films were chemically modified by immersing them in a dry acetonitrile solution of 3-aminopropyl triethoxysilane. When the surface amino groups of the modified opal films are protonated and there is little or no supporting electrolyte present in solution, the flux of cationic redox species through the opal membrane is blocked because of electrostatic repulsion. The permselectivity is pH-dependent and can be modulated by adjusting the Debye screening length within the nanopores of the opal by changing the ionic strength of the contacting solution.

Introduction

Synthetic opals form via self-assembly of submicrometer-sized silica spheres into a close-packed face-centered cubic (fcc) lattice with a void fraction of 0.26 independent of the size of the spheres.¹ Opals contain highly ordered arrays of 3D interconnected pores, approximately 15–80 nm in size for opals assembled from 100- to 500-nm-diameter spheres. Opal films are ideal candidates for highly selective nanoporous membranes. The diffusive flux of small molecules normal to the (111) plane of an infinitely thick opal layer is only ca. 10 times smaller than the free solution value, independent of the size of the spheres used to synthesize the opal.² Thus, the molecular flux through opals remains significant even when the pore size is sufficiently small to impart chemical selectivity.² In addition, the chemical modification of the opal surface is facile.^{3,4}

Recently, we described chemically modified thin nanoporous opal films functioning as ion-selective pH-responsive membranes.⁵ Simultaneously, Ozin et al. reported on polystyrene-based colloidal crystal capillary columns for optical chromatography,⁶ and Wirth et al. described the electromigration of DNA molecules through an opal film with a high electrophoretic mobility.⁷ Earlier, pH-switchable selectivity was demonstrated for the transport of ions in gold nanotubes using chemisorbed L-cysteine⁸ and for the transport of ions to an electrode surface using ultrathin films^{9,10} and self-assembled monolayers.¹¹

In our previous report, we demonstrated that a thin opal film comprising three layers of 440-nm-diameter silica spheres can

be chemically modified with surface amino groups. At pH lower than the pK_a of the surface-bound amines,¹² the transport of positively charged species in the opal films was impeded whereas the transport of negatively charged and neutral species was unaltered.⁵ In the present report, we describe our investigation of the mechanism underlying the observed permselectivity by measuring the molecular fluxes of several neutral and charged redox molecules through the amine-modified opal films as a function of the solution ionic strength and pH. We demonstrate that the permselectivity is based on electrostatic repulsion and can be modulated by adjusting the Debye screening length within the pores of the opal film.

Experimental Section

Materials. Hexaamineruthenium(III) chloride, $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ (99%, Strem Chemicals), potassium ferrocyanide(II) trihydrate, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot (\text{H}_2\text{O})_3$ (99%, Aldrich), potassium chloride (99%, Mallinckrodt), potassium hexachloroiridate(III), K_3IrCl_6 (98%, Aldrich), 3-aminopropyl triethoxysilane (98%, Aldrich), trifluoroacetic acid (99%, Acros), tetra-*n*-butylammonium hexafluorophosphate (98%, Alfa Aesar), 1,1'-ferrocenedimethanol (98%, Aldrich), and bis(cyclopentadienyl)iron (99%, Alfa Aesar) were used as received. Iron trisbipyridine hexafluorophosphate, $\text{Fe}(\text{bpy})_3(\text{PF}_6)_2$, was synthesized according to literature procedures.^{13–15} Acetonitrile (Mallinckrodt, HPLC grade) was used after being freshly distilled from CaH_2 . Triethylamine (98%, J. T. Baker) was distilled from CaH_2 before use.

Silica spheres were synthesized^{16–19} by adding 0.2 M tetraethyl orthosilicate (TEOS) in absolute ethanol to a solution of 1.1 M ammonia and 17 M water in absolute ethanol. The mixture was stirred for 24 h at room temperature. Silica spheres were collected and purified by repeated centrifugation in absolute ethanol. The diameter of the spheres was determined to be 440 ± 11 nm using scanning electron microscopy (SEM).

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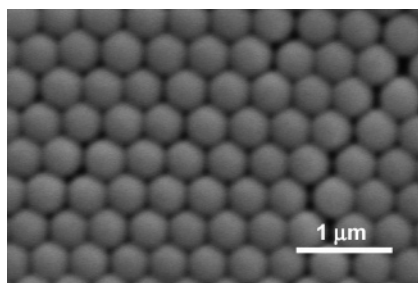


Figure 1. SEM images of a chemically modified opal film prepared from 440 nm silica spheres (top view) as described in the text.

Pt Microdisk Electrodes. Pt microdisk electrodes (25 μm in diameter) shrouded in glass were prepared by first attaching a 1.0-mm-diameter Cu wire (Alfa Aesar) to a 25- μm -diameter Pt wire using Ag paint (DuPont). The Pt wire was then flame sealed in a glass capillary; the capillary was bent into a U-shape, and the middle was cut orthogonal to the length of the capillary with a diamond saw to expose the Pt disk. The resulting electrodes were then polished with Microcut Paper disks (Buehler), from 240 to 1200 grit in succession, until the surface was free from visible defects.

Amine-Modified Opal Films. Opal films were deposited on the electrode surfaces by placing the electrodes vertically²⁰ in a 1.5 wt % colloidal solution of silica spheres in ethanol and letting the solvent evaporate for 2 to 3 days in a vibration-free environment. The 1.5 wt % silica spheres solution produced three-layer films, as was shown by SEM.⁵

The surface of the spheres, after assembly into opal films on the Pt electrode, was chemically modified with amines by immersing the electrode under nitrogen in dry acetonitrile containing 0.056 M 3-aminopropyl triethoxysilane (APTES) for 17 h at room temperature. After modification, the electrodes were soaked and rinsed in dry acetonitrile. A representative image (top view) of a chemically modified opal film is shown in Figure 1.

A small number of opal-modified Pt electrodes had to be discarded because of the cracking of the opal film, but a majority of the electrodes, both before and after the opal surface modification, were stable and reusable.

Voltammetric Measurements. The flux of permeants across the opal film was measured voltammetrically using a two-electrode cell and an Ag/AgCl reference/counter electrode. A Par model 175 universal programmer and Dagan Cornerstone Chem-Clamp potentiostat were used to conduct the measurements. Data were recorded with a PC using programs written in LabView. Aqueous solutions were prepared using 18 M Ω ·cm water obtained from a Barnstead "E-pure" water purification system. All acetonitrile solutions were prepared with dry acetonitrile. All solutions were purged with N₂ to remove dissolved O₂. The pH of the aqueous solutions was adjusted by the addition of acetic acid and sodium hydroxide. Trifluoroacetic acid and triethylamine were used to adjust the acidity of acetonitrile solutions. The following concentrations of redox species were used: 5.1 mM Ru(NH₃)₆³⁺, 5.2 mM Fe(CN)₆⁴⁻, 1.6 mM Fc(CH₂OH)₂, 2.0 mM IrCl₆³⁻, 5.0 mM Cp₂Fe, and 3.0 mM Fe(bpy)₃²⁺.

Computer Simulations. Finite-element simulations were performed using Femlab 2.0 software (Comsol, Inc.) using a Dell Dimension SP (Pentium-4 CPU, 3.2 GHz, 2 GB of RAM).

Results and Discussion

Effect of Opal Film Thickness on the Molecular Flux. Figure 2 shows the voltammetric responses of 25- μm -diameter Pt microdisk electrodes prior to and following the deposition of three layers of 440 nm silica spheres in aqueous and acetonitrile solutions containing six redox couples: two neutral molecules, two multiply charged anions, and two multiply charged cations. The voltammetric responses for each redox species display a

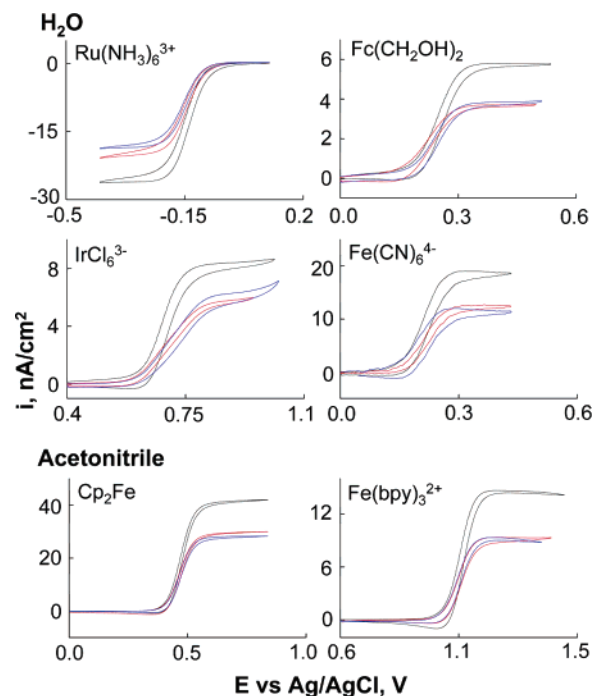


Figure 2. Voltammetric responses of a 25- μm -diameter Pt electrode: bare (black), after opal assembly (red), and after chemical modification of the opal membrane with APTES (blue) at neutral pH.

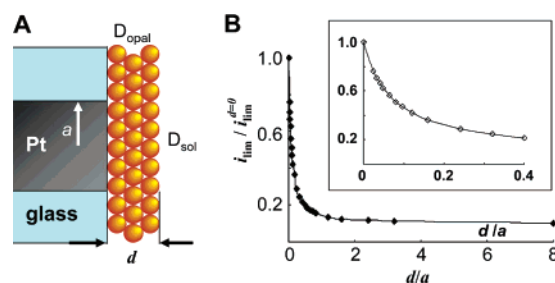


Figure 3. (A) Model of an opal film on a Pt microdisk electrode. The opal is treated as a homogeneous phase in which the diffusivity of redox molecules in the opal (D_{opal}) is less than the diffusivity in the bulk solution (D_{sol}). (B) Plot of the normalized limiting current at an opal-modified electrode ($i_{\text{lim}}^{d=0}/i_{\text{lim}}^d$) vs the normalized opal thickness (d/a) for a 25- μm -radius electrode. (Inset) Magnified region of B for very thin opal films.

sigmoidal shape characteristic of near-steady-state radial diffusion of the redox species to a microelectrode.²¹ Following deposition of the opal film onto the Pt electrode, an $\sim 30\%$ reduction in the limiting current (i_{lim}) is observed (Figure 2), irrespective of the solvent and redox species.

A previous investigation in our laboratory determined that the effective diffusivity of molecules through an infinite opal lattice (D_{opal}) is approximately 10 times smaller than the corresponding bulk solution value (D_{sol}), a consequence of the reduced volume available for diffusion and the tortuosity of the diffusional path.² To estimate the decrease in i_{lim} expected at an electrode coated with a finite-thickness opal film, we conducted finite-element simulations. As depicted in Figure 3A, the simulation model consisted of a Pt microdisk of radius a , coated with an opal of thickness d , and immersed in a large volume of solution containing a redox-active species. The effect of the tortuous pathway within the opal on diffusion was determined in our previous study of

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an infinitely thick (111)-oriented lattice of spheres and was included in the present simulations.² Specifically, we modeled the opal layer as a homogeneous phase in which redox species undergo Fickian diffusion with a diffusivity D_{opal} . Finite-element simulations using Femlab were performed to obtain the diffusive flux (J_{opal}) of redox species from the bulk solution to the electrode assuming instantaneous electron transfer at the Pt surface. This flux corresponds to the voltammetric limiting current, $i_{\text{lim}} = nFAJ_{\text{opal}}$ (where n is the number of electrons transferred per molecule, F is the Faraday constant, and A is the area of the Pt electrode).

Figure 3B (and inset) shows a plot of the dependence of the normalized voltammetric limiting current ($i_{\text{lim}}/i_{\text{lim}}^{d=0}$) on the normalized opal thickness (d/a). The precipitous drop in $i_{\text{lim}}/i_{\text{lim}}^{d=0}$ with increasing d/a , approaching a constant value for $d/a > 1$, is readily understood in terms of the quasi-radial flux of redox species to a disk-shaped microelectrode. The radial flux is limited by the largest resistance to diffusive transport which occurs in the region of space immediately adjacent to the electrode surface (within ~ 1 radius of the surface). Thus, because the diffusivity within the opal film is approximately 10 times smaller than in bulk solution, the deposition of even a very thin opal layer results in a significant decrease in $i_{\text{lim}}/i_{\text{lim}}^{d=0}$. The limiting current approaches an asymptotic value equal to $D_{\text{opal}}/D_{\text{sol}} = 0.1$ when the opal layer thickness is greater than ca. 1 radius because the diffusional resistance associated with radial transport decreases in inverse proportion to distance from the electrode.¹⁸

In our experiments, the opal thickness is equal to $\sim 1 \mu\text{m}$, thus $d/a = 1 \mu\text{m}/12.5 \mu\text{m} \approx 0.08$. Therefore, the predicted value of $i_{\text{lim}}/i_{\text{lim}}^{d=0}$ is ~ 0.55 (Figure 3B), in reasonable agreement with the value of 0.7 (Figure 2) observed for unmodified opal films. A slight decrease in current observed after modification of the opal membrane with APTES may be due to the formation of a thin polymeric layer on the silica sphere surfaces, which would decrease the size of the pores within the opal.

pH Effect on Diffusion through Amine-Modified Opal Films. The limiting current, i_{lim} , was used as a measure of the molecular flux through the opal films. Figure 4 shows the voltammetric responses of amine-modified Pt/opal electrodes in water and acetonitrile in the presence of acid. As clearly seen in Figure 4, neutral and negatively charged species diffuse freely across both the unmodified and amine-modified opal films under these conditions. However, the fluxes of $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Fe}(\text{bpy})_3^{2+}$ are reduced to nearly background levels after the addition of acid. The modulation of flux through amine-modified opal films is reversible, as shown in Figure 5. Thus, when the opal film surface is neutralized by placing the electrode in either sodium hydroxide solution in water or triethylamine solution in acetonitrile, the film becomes permeable for the diffusion of $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Fe}(\text{bpy})_3^{2+}$, respectively (Figure 5). If the surface is protonated again, then the blocking is restored with the original magnitude. This cycling has been repeated four times for twenty different electrodes without the loss of blocking.

When voltammetric measurements were conducted for unmodified opal films at pH 10, where the hydroxyl groups on the surface of the silica spheres are deprotonated and negatively charged,^{22,23} a small decrease in limiting current (ca. 10%) was observed for IrCl_6^{3-} oxidation. The influence of negative surface charge in the deprotonated and unmodified opal films on negatively charged species is much smaller compared to the

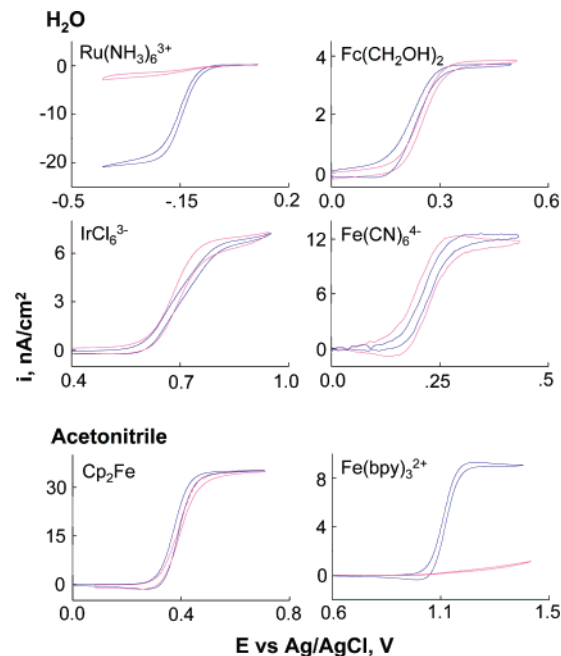


Figure 4. Voltammetric responses of the Pt electrode after opal assembly (blue) and after chemical modification of the opal membrane with APTES (magenta) at pH ~ 4 (water) and in a 0.36 mM solution of trifluoroacetic acid in acetonitrile.

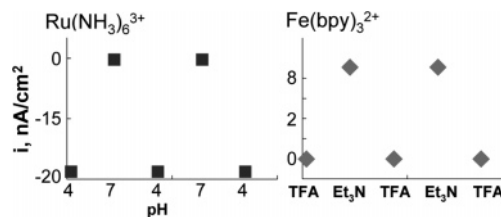


Figure 5. Reproducibility of the limiting current values measured for the Pt electrode coated with an amine-modified opal film for $\text{Ru}(\text{NH}_3)_6^{3+}$ in water and $\text{Fe}(\text{bpy})_3^{2+}$ in acetonitrile in the presence and absence of acid.

effects in the protonated amine-modified opal films on the positively charged species. The enhanced influence of the positive surface charge may be due to the presence of a thin polymeric film that contains a larger number of charged protonated amines. The surface negative charge could not be further increased by increasing the solution pH beyond 10 because this led to the degradation of the silica opal film. We are presently studying the pH-dependent transport of anions through opals modified with polymeric films containing carboxylic groups.

Ionic Strength Effect on Diffusion through Amine-Modified Opal Films. To demonstrate that the permselectivity in amine-modified opal films is electrostatic in nature, we studied the diffusion of $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Fe}(\text{bpy})_3^{2+}$ through the films as a function of solution ionic strength. All tests were conducted with $\text{Ru}(\text{NH}_3)_6^{3+}$ and KCl in water or with $\text{Fe}(\text{bpy})_3^{2+}$ and tetrabutylammonium hexafluorophosphate in acetonitrile. At low pH in water or in the presence of trifluoroacetic acid in an acetonitrile solution and with no supporting electrolyte in solution, the flux is essentially zero (Figure 6). Increasing the electrolyte concentration increases the flux for both positive species, $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Fe}(\text{bpy})_3^{2+}$ (Figure 6).

These observations clearly demonstrate the electrostatic nature of the permselectivity. Indeed, as electrolyte is added to the solution, it screens the charge of the surface ammonium groups, allowing the positively charged species to diffuse through the opal film. However, the degree of permselectivity appears to be

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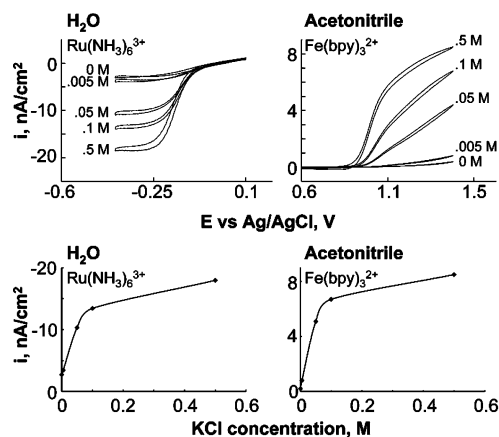


Figure 6. Voltammetric responses of the protonated amine-modified Pt/opal electrode for $\text{Ru}(\text{NH}_3)_6^{3+}$ reduction in water and $\text{Fe}(\text{bpy})_3^{2+}$ oxidation in acetonitrile as a function of KCl concentration. KCl concentrations are shown adjacent to each voltammogram.

larger than that anticipated on the basis of electrostatic interactions alone. For instance, for the opal comprising 440 nm silica spheres the distance from the center of the pore to the nearest sphere surface is ca. 35 nm. Within this structure, an $\sim 50\%$ blocking of diffusion is observed at an electrolyte concentration of 0.05 M (Figure 6), where the Debye screening length (κ^{-1}) is only ca. 1.5 nm. Assuming that the electric field extends $\sim 5\kappa^{-1}$ from the surface (~ 7.5 nm, corresponding to the distance where the potential decays to $\sim 1\%$ of the surface potential), the electric field extends over only a small fraction ($\sim 22\%$) of the effective pore width. This evaluation is highly approximate and probably underestimates the electrostatic effect due to the noncylindrical pores in the opal being effectively smaller than the distance between the center of the pore and sphere surface (~ 35 nm) employed in the analysis above. We speculate that the tortuous path that molecules take to diffuse through the opal film to reach the electrode, the finite thickness of amine layer, and the high surface area of the opal contribute to enhancing the observed electrostatic permselectivity.

Chemical Selectivity in Diffusion through Amine-Modified Opal Films. Electrodes coated with an amine-modified opal film can be used to detect redox-active species selectively on the basis of their charge. To demonstrate this ability, neutral and positively charged species with different $E_{1/2}$ values were placed

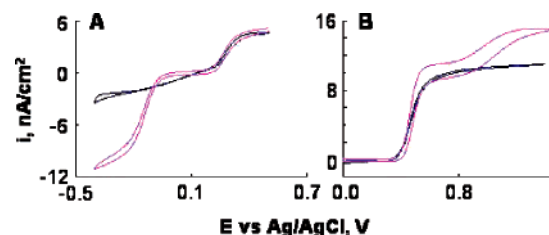


Figure 7. (A) Voltammetric response of $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Fc}(\text{CH}_2\text{OH})_2$ in H₂O at pH ~ 4 (black) and pH ~ 9 (magenta). (B) Voltammetric responses of $\text{Fe}(\text{bpy})_3^{2+}$ and ferrocene in acetonitrile with 0.36 mM trifluoroacetic acid (black) and after treatment with triethylamine (magenta).

in either aqueous or acetonitrile solution in the presence of an acid. For example, in an aqueous solution containing $\text{Ru}(\text{NH}_3)_6^{3+}$ and the neutral redox species dimethanolferrrocene ($\text{Fc}(\text{CH}_2\text{OH})_2$), only the neutral species diffuses to the electrode and is detected at low pH, as indicated by the lack of a voltammetric wave for $\text{Ru}(\text{NH}_3)_6^{3+}$ reduction and the presence of a wave for $\text{Fc}(\text{CH}_2\text{OH})_2$ oxidation (Figure 7A). Deprotonation of the films at high pH allowed the diffusion of both the positively charged and neutral species, as indicated by the reappearance of the wave for $\text{Ru}(\text{NH}_3)_6^{3+}$ reduction. Similar results were obtained for $\text{Fe}(\text{bpy})_3^{2+}$ and ferrocene in acetonitrile, as shown in Figure 7B.

Conclusions

We demonstrated that the permselectivity for the transport of positively charged species through amine-modified opal films at low pH is based on electrostatic repulsion and is modulated by the Debye screening length of the electric field within the pores of the opal film. In the absence of a supporting electrolyte, nearly ideal permselectivity can be achieved. Pt electrodes coated with amine-modified opal films can be used at low pH to detect neutral redox species selectively in the presence of positively charged redox species.

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