

## Chemically Modified Opals as Thin Permselective Nanoporous Membranes

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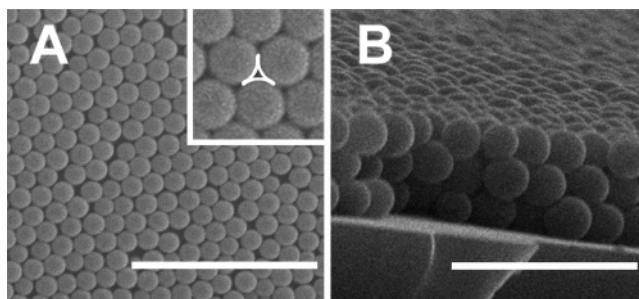
Nanoporous membranes capable of selectively separating molecules are attractive targets in fundamental research and technology.<sup>1</sup> A number of novel nanoporous membranes have been recently prepared using self-assembled polymeric films,<sup>2</sup> zeolites,<sup>3</sup> silicon nitride films,<sup>4</sup> and nanotubes.<sup>5,6</sup> An ideal separation membrane contains pores whose size and surface chemistry can be easily controlled to impart selectivity for a wide range of separations, while simultaneously maintaining high transport rates of desired molecules. Herein, we report on using thin opal films as such a platform.

Synthetic opals are used as templates for preparing photonic materials,<sup>7,8</sup> energy storage media,<sup>9</sup> magnetic materials,<sup>10</sup> macroporous polymer membranes,<sup>11,12</sup> and sensors.<sup>13</sup> Opals comprise a close-packed face center cubic (fcc) lattice of silica spheres of sub-micrometer diameter, with a void fraction of 0.26.<sup>14</sup> Molecules diffusing within an opal follow a tortuous path through the lattice of spheres, impeding transport through the opal. However, the diffusive flux of small molecules normal to the (111) plane of a bulk close-packed fcc lattice of silica spheres is only ca. 10 times smaller relative to the free solution value, independent of the size of the spheres used to synthesize the opal.<sup>15</sup> Thus, the molecular flux through opals remains significant, even when the pore size is reduced to sufficiently small scales to impart chemical selectivity.

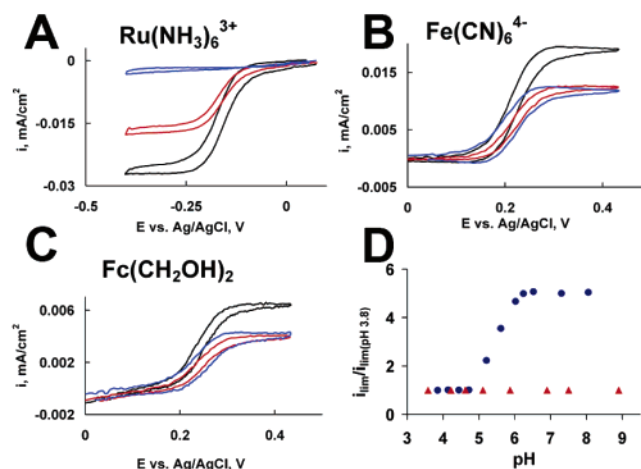
The preparation of silica spheres is straightforward.<sup>16</sup> Self-assembly of the spheres into opal films is well developed,<sup>17</sup> pore size in the opal film can be easily controlled by selecting the sphere size, and silica surface chemistry is well established.<sup>18</sup> These features, in combination with high transport rates, make opal films ideal candidates for highly selective nanoporous membranes. To demonstrate that an opal film can indeed work as a permselective membrane, we modified the surface of silica spheres with amino groups, with the goal of imparting pH-dependent permselectivity based on electrostatic interactions between the protonated amino groups and charged permeants.

To prepare chemically modified opal films, we first assembled the thin-film opals, made of  $440 \pm 11$  nm silica spheres,<sup>19</sup> on the surface of  $25 \mu\text{m}$  radius disk-shaped Pt microelectrodes, shrouded in glass and vertically oriented. Chemical modification of the opal membranes was achieved by the treatment with 3-aminotriethoxysilane.<sup>19</sup> A representative SEM picture of a three-layer-modified opal film deposited on the Pt electrode is shown in Figure 1. It is likely that a thin polymeric layer is formed on the silica spheres surface, but no evidence of the formation of thick polymeric layers is seen in the SEM images.<sup>20</sup>

The permselectivity of the chemically modified opal films was determined by measuring the flux of redox-active molecules across the opal in quasi-steady-state voltammetric experiments.<sup>21</sup> To separate the effects of the lattice tortuosity and surface chemistry on the molecular flux, voltammograms were recorded for (i) the bare electrodes, (ii) the electrodes after the opal self-assembly, and (iii) the electrodes after chemical modification of the opal membrane with 3-aminotriethoxysilane. Figure 2 shows the voltammetric responses of a Pt electrode in aqueous solutions of either 5.1 mM



**Figure 1.** SEM images of the chemically modified opal prepared from 440 nm diameter silica spheres deposited (A) on the electrode, top view (size bar =  $4 \mu\text{m}$ ); and (B) on a glass slide under the same conditions, side view (size bar =  $2 \mu\text{m}$ ). The geometric projection of a pore observed from the (111) plane is outlined in the inset in (A).



**Figure 2.** (A–C) Voltammetric responses of a Pt electrode: bare (black), after opal assembly (red), and after chemical modification of the opal thin film with 3-aminotriethoxysilane (blue). (D) Voltammetric responses of a Pt electrode as a function of pH for unmodified (red triangles) and modified (blue circles) opal film electrode.

$\text{Ru}(\text{NH}_3)_6^{3+}$ , 5.2 mM  $\text{Fe}(\text{CN})_6^{4-}$ , or 1.6 mM  $\text{Fc}(\text{CH}_2\text{OH})_2$  and 0.2 M KCl as supporting electrolyte. The voltammetric response of the bare electrode for each redox species (Figure 2) displays a sigmoidal shape characteristic of radial transport to a microelectrode.<sup>22</sup> The limiting current ( $i_{\text{lim}}$ ) is proportional to the bulk solution diffusivity of the respective molecules.<sup>23</sup>

Following deposition of the opal thin film, similar sigmoidally shaped voltammetric responses were obtained, but with a  $\sim 30\%$  reduction in  $i_{\text{lim}}$  for all molecular species (Figure 2A–C). The reduction in current for the opal-modified electrode, prior to chemical modification, is due solely to geometrical effects associated with the meandering path that the redox molecules take when diffusing through the opal lattice. The reduction in flux (a factor of  $\sim 1.5$ ) is lower compared to that in a thick opal layer (a factor of  $\sim 10$ )<sup>15</sup> due to the thinness of the three-layer opal ( $\sim 0.001$  mm). Such a thin layer, however, has a significant physical blocking

effect in our experiment, a consequence of the convergent flux of redox molecules to the microelectrode that produces a nonlinear decrease in the mass transport resistance with increasing distance from the surface.<sup>22</sup>

Permselective behavior is readily apparent in the voltammetric response of the electrode after covalent attachment of amino groups to the silica spheres. At pH  $\sim 4$ , the voltammetric limiting current,  $i_{lim}$ , corresponding to the one-electron reduction of  $Ru(NH_3)_6^{3+}$  is greatly diminished (Figure 2A), while  $i_{lim}$  for the one-electron oxidations of  $Fe(CN)_6^{4-}$  and  $Fe(CH_2OH)_2$  remains approximately the same as before surface modification (Figure 2B,C). This result is consistent with electrostatic repulsion of the cationic species,  $Ru(NH_3)_6^{3+}$ , by protonated surface amines.

To verify that the permselectivity results from the chemical modification of the opal and not the Pt electrode surface, we treated the bare Pt electrodes with 3-aminotriethoxysilane in dry acetonitrile. The treated electrodes did not show any permselective behavior. In addition, opal membranes prepared from silica spheres modified in solution *prior to the opal assembly* also showed permselective behavior.

To demonstrate that the permselectivity arises from electrostatic interactions involving the amine surface functionality, we recorded the voltammetric limiting current for  $Ru(NH_3)_6^{3+}$  reduction as a function of pH. Figure 2D shows a plot of the voltammetric limiting current<sup>24</sup> recorded at different pH's. The flux of  $Ru(NH_3)_6^{3+}$  increases sharply beginning at pH 5 and rises by a factor of 3–5 as the pH is increased to a value of 7. Above this pH,  $i_{lim}$  remains constant. The sigmoidal shape of the normalized plot of  $i_{lim}/i_{lim(pH3.8)}$  versus pH is consistent with  $RNH_2/RNH_3^+$  equilibrium with a  $pK_a$  of  $5.7 \pm 0.2$  (based on four independent measurements). This value is significantly lower than the solution  $pK_a$  of alkylammonium ions ( $\sim 10$ ), but it is consistent with the low  $pK_a$  values reported for surface-bound alkylammonium species and attributed to electrostatic repulsion between neighboring alkylammonium groups, resulting in their deprotonation at lower pH.<sup>25</sup> The dependence of voltammetric limiting current for  $Ru(NH_3)_6^{3+}$  reduction on the solution pH was also measured for Pt electrodes coated by thin layers of *unmodified* silica spheres. No change in  $i_{lim}$  was observed as the pH was varied (Figure 2D), confirming that the flux in the lattice of modified spheres is controlled by the  $RNH_2/RNH_3^+$  equilibrium.

Furthermore, we studied the dependence of the permselectivity upon supporting electrolyte concentration. For modified opal membranes at neutral pH, increasing the electrolyte concentration led to a small decrease in the  $Ru(NH_3)_6^{3+}$  limiting current, a consequence of the electrolyte reducing the electrical field (and resulting ion migration) engendered by reduction of  $Ru(NH_3)_6^{3+}$ .<sup>22</sup> Conversely, at low pH, increasing the electrolyte concentration led to a large *increase* in the limiting current. We interpret the latter dependence as being due to screening of the positively charged surface ammonium groups by the electrolyte ions that "opens" the pores for the diffusion of  $Ru(NH_3)_6^{3+}$ .

The distance between the center of a pore and the surface of the nearest spherical surface ( $\sim 35$  nm) is large in comparison to the distance that electrostatic fields extend from the surface protonated amines ( $\sim 5 \kappa^{-1} = \sim 4$  nm, where  $\kappa^{-1}$  is the Debye length in our experiment). Thus, molecules in the center of the pore are not

expected to electrostatically interact with the pore surface. This suggests that the electrostatic interactions are enhanced by the tortuous pathway within the opal and by the high surface area of the chemically modified spheres.

The above preliminary experiments demonstrate two properties of opal-based membranes that are important in chemical separations: (i) selectivity and (ii) high molecular throughput. We are presently working on further elucidating the permselectivity mechanism and on more selective opal-based membranes prepared by combining spheres with different surface functional groups.

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**Supporting Information Available:** Details of the experimental procedures and SEM images of the modified opal membranes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (20) Extended (2–3 days) treatment with 3-aminotriethoxysilane resulted in complete blocking of nanopores, as was evident from the loss of the electrode signal and from SEM images (see Supporting Information).
- (21) Permselectivity of molecular and polymer films has been previously investigated by electrochemical methods (Naegeli, R.; Redepenning, J.; Anson, F. C. *J. Phys. Chem.* **1986**, *90*, 6227–6232. Redepenning, J.; Anson, F. C. *J. Phys. Chem.* **1987**, *91*, 4549–4553).
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- (23) In the steady-state voltammetric experiment,  $i_{lim}$  is proportional to the molecular flux in the opal layer,  $J_{opal}$  (i.e.,  $i_{lim} = nFAJ_{opal}$ , where  $n$  is the number of electrons transferred per molecule,  $F$  is Faraday's constant, and  $A$  is the electrode area).<sup>22</sup>
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