A Potential Separation Method for Polycyclic Organic Compounds Based on Gold Nanotube Membranes

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Introduction

Many of the environmental endocrine disruptors such as pesticides, PCBs, PAHs, phathalate esters, phenolics etc have polycyclic structure, and the separation and analysis of these species in different environmental matrices has been a major challenge to the analytical chemists. In this paper, a new separation medium based on gold nanotubules has been developed and its performance as a separation membrane towards polycyclic species has been evaluated. The gold nanotube membranes were fabricated within the template polycarbonate membranes by electroless gold deposition and modified by L-cysteine and guanidine thiocyanate through self-assembling within about 0.2nm in the I.D. of the nanotubes. The fabrication of nanomaterialsoffered interesting possibilities as a noval separation media besides other applications ascatalysts, sensors, and nanoelectronic devices. Several polycyclic molecules were selected as the permeants and their transport behavior in four different membranes, namely, polycarbonate membranes, gold nanotubule membranes, L-cysteine modified and guanidine thiocyanate modified gold nanotubule membranes have been investigated. The selected species include fluorescein, fluorescein sodium, dichlorofluorescein, fluoresceinisothiocyanate and lactoflavine. The results show that thefluxes of fluorescein sodium, dichlorofluorescein, fluoresceinisothiocyanate through the membranes do not vary much whereas the flux of lactoflavine through modified nanotube membranes is much faster than that of fluorescein. The gold nanotube membranes thus have the potential to be further developed as an effective technique for the separation of polycyclic organic pollutions.

Experimental

Materials. Track-etched polycarbonate (PC) membranes with monodiperse pores were bought from Millpore as the substrates for electroless deposition of gold. The membranes have a hydraulic pore radius of 50nm, a pore density of 6 pores/μm^2, and a thickness of 6-8 μm. The chemicals, $SnCl_2 \cdot H_2O$, $AgNO_3$, auric chloride acid, trifluoroacetic acid, L-cysteine hydrochloride (AMERSCO), guanidine thiocyanate (AMERSCO), fluorescein, fluorescein sodium, dichlorofluorescein, fluoresceinisothiocyanate and lactoflavine are of analytically pure. Ultrapurified water (18.2MΩ) was obtained by passing house-distilled water through a high-purification system (Millpore) and used for preparation of all solutions and for rinsing.

Preparation of the membranes. Gold electroless deposition on the inner pore walls and both faces of the PC membranes was achieved under ambient conditions through a chemical autocatalytic plating process including chemical cleaning, chemical sensitizing, activation and deoxidization. L-cysteine hydrochloride and guanidine thiocyanate were dissolved in ethanol to obtain a 5mM solution. The chemisorptions of L-cysteine and guanidine thiocyanate were accomplished by immersing the gold membranes into the modifier solution for 24 hours with N_2 purging. The gold coated membranes were then rinsed with ethanol and dried in air. Measurements taken by Martin have proved that after chemisorption of the modifiers there was a slight decrease (0.2 nm) in the I.D. of the gold membrane.

Permeants transport. The PC membranes (PC-Mem), gold nanotubule membranes (Au-Men), L-cysteine modified gold nanotubule membranes (Cys-Au-mem) and guanidine thiocyanate modified gold nanotubulemembranes(gua-au-Mem) were mounted between two halves of a U-pool cell. A 10 mm diameter O-ring held the membrane in place and defined the effective area of the membrane exposed to the feed cell and the permeant half-cell solutions. The feed half-cell contained 20 ml of an aqueous of the permeant molecule to be transported and the other half-cell initially contained 20ml of the same solvent as of the feed half-cell. The transport of the permeant molecule into the

permeant half-cell was monitored by periodically assaying (via fluorescence spectrum) the permeant solution. And these membranes showed reproductive fluxes for 3times.

Results and discussion

Single molecule transport. We first investigated the effect of hydrophobic property of single permeant molecule on its transport through the nanoporous membranes of 12 hours deposition with 25-nm-diameter pores.

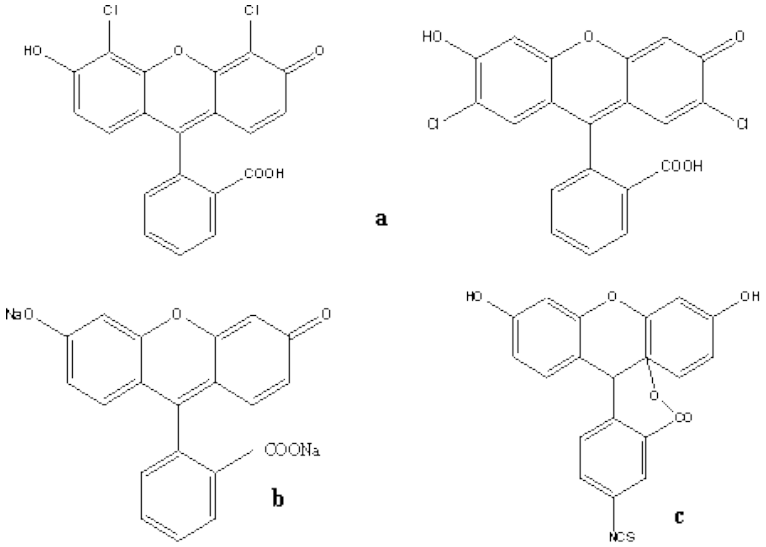

Fig. 1 Structures of the permeants: dichlorofluorescein (a), fluorescein sodium (b) and fluorescein isothiocyanate (c)

Table 1 showed the transporting rates of dichlorofluorescein (DFL), fluorescein sodium (FLNa) and fluoresceinisothiocyanate (FITC)in permeate cell with a time duration of 3 days. Two observations are noted: (1) the permeating rate for the 3 chemicals through different nanotube membranes were not the same. FITC transferred more rapidly through the 3 kinds of nanotube membranes than those of DFL and FLNa., and (2) For every chemical, the highest permeating rate was observed in Cys-Au-Mem. The results suggest that the hydrophobic and the

interaction of the chemicals with the nanotubes may play important roles in the performance of transporting.

Table 1 Permeating rates of the 3 chemicals after 3 days

	Au-Mem (25nm)	PC-Mem (50nm)	Cys-Au-Mem (25nm)	hydrophobic
FLNa	3.22	4.47	6.81	A-
DFL	4.33	7.22	7.98	A+1.42
FITC	7.49	7.92	10.33	A+0.41

To test further the effect of hydrophobicity on transport, two probe molecules lactoflavine and fluorescein were selected for comparison. The two differ in both hydrophobicity and degree of conjugation as illustrated by the structures given in Figure 2, . Such differences should result in difference in transporting activities across the modified nanotube membranes, and the supposition was confirmed by the data shown in Figure3.

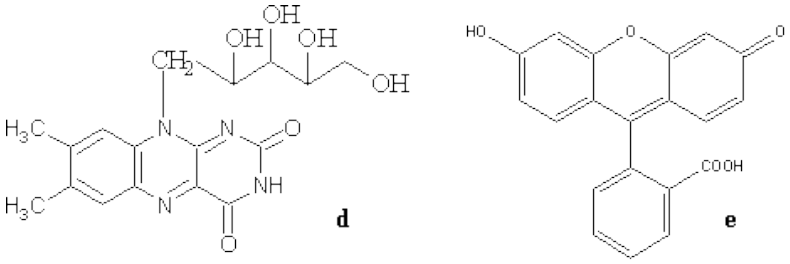

Fig. 2 Structures of the membrane material d, lactoflavine; and e fluoresciein

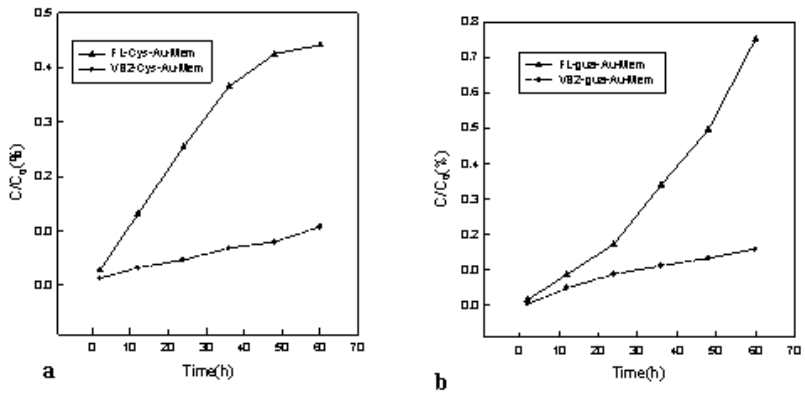

Fig. 3 tranaporting plots of lactoflavine (VB2)and fluoresciein (FL) through the cysteine and carbamidine thiocyante modified gold nanotubules (Cys-Au-Mem, gua-Au-Mem) versus time a. cysteine (Cys) modified; b. carbamidine thiocyante (gua)

In both L-cysteine or guanidine thiocyanate modified membranes, fluorescein transported faster than lactoflavine. In addition, the relative permeating rate obtained by dividing the concentration flux in permeating cell offluorescein by that of lactoflavine is higher in gua-Au-Mem (47.2) than in Cys-Au-Mem(40.8). The former membrane thus has better selectivity as a transport medium.

Conclusions

The permeating rates of fluorescein, fluorescein sodium, dichlorofluorescein, fluoresceinisothiocyanate and lactoflavine through polycarbonate membranes, gold nanotubule membranes, L-cysteine modified gold nanotubule membranes and guanidine thiocyanate modified gold nanotubule membranes have been studied and compared. The results showed that both hydrophobic and physiochemical interactions between the chemicals and the nanotubes influence the transporting activities of polycyclic organic compounds. Gold nanotube membranes show promising potential as an effective separation medium for environmental endocrine disruptors having various polycyclic structures.

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