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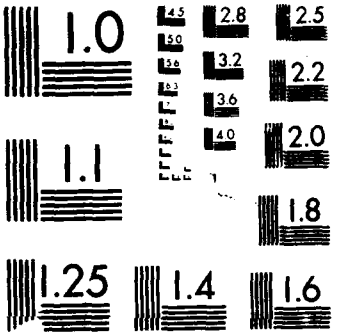
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Transparent Metal Microstructures

Michael J. Tierney and Charles R. Martin*

Department of Chemistry
Texas A&M University
College Station, TX 77843

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ABSTRACT

Metal films with thicknesses greater than several hundred angstroms are usually opaque. Effective medium theory predicts, however, that electrically disconnected metal microcylinders with diameters small relative to the wavelength of the impinging light will be transparent. In this correspondence, we describe the synthesis and optical characterization of ensembles of such small (200 nm-dia) metal microcylinders. We show that, in agreement with the predictions of effective medium theory, these microstructures are highly transparent.

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INTRODUCTION

Metal films with thicknesses greater than several hundred angstroms are usually opaque. Effective medium theory predicts, however, that electrically disconnected metal particles which are small relative to the wavelength of the impinging light will be transparent (1-3). Transparency results because the optical electric field causes a screening charge to develop on the surfaces of the particles; this screening charge excludes the electric field from the particles and "squeezes" the photons into the surrounding void space (1-3).

Heller et al. have recently demonstrated this effect using photoelectrochemically deposited metal films (2,3). These films were composed of small and (partially) electrically disconnected particles. As discussed in detail by Heller et al., this microstructure is not optimal (3). For an unpolarized light source, the optimal microstructure is an ensemble of cylinders in which the axes of the cylinders are parallel to the incident light rays (3).

We have recently described an electrochemical procedure for preparing ensembles of parallel metal microcylinders (4). The above discussion indicates that these ensembles should function as transparent metal "films." We have investigated the optical properties of an ensemble of 200 nm-diameter gold microcylinders and have shown that these cylinders are highly transparent. We report the results of these studies in this correspondence.

EXPERIMENTAL

The general synthetic strategy entails electrochemical deposition of Au into the pores of a microporous filtration membrane (4); the pores act as templates for the nascent Au microcylinders. Anopore (Alltech Associates)

microporous membranes were employed. Anopore is an Al_2O_3 membrane with parallel 200 nm-diameter pores and a fractional pore surface area of ca. 65 percent. The following microfabrication procedure was used to prepare the ensembles of Au microcylinders.

A thin (30 nm) layer of Ag was sputtered onto one side of the Anopore membrane. This layer did not cover (i.e. plug) the pores but served to convert the surface of the Anopore membrane into an electrode. Ag epoxy was used to make electrical contact with this surface layer. The Ag-coated membrane was then immersed into a Ag plating solution using the cell shown in Figure 1. (Note that this cell exposes only the Ag-coated surface to the solution.) Ag was deposited galvanostatically (current density = 1.25 mA-cm^{-2}, time = 125 min) at the Ag/Anopore surface. This electrochemical deposition step left a thick (ca. 10 μm) Ag film on the surface of the membrane. This thick Ag layer completely covered and sealed the pores.

The Ag/Anopore membrane was removed from the electrochemical cell (Figure 1) and rotated 180° so that the bare Anopore side was facing the solution and the Ag-covered side was facing the cell wall. Ag was deposited into the pores, forming microcylinders 1 to 2 μm in length. At this point, the Ag/Anopore membrane appeared as shown schematically in Figure 2A. Au was then plated potentiostatically (E = -0.9 V vs. Ag/AgCl) onto the Ag microcylinders (Figure 2B). The Au/Ag/Anopore composite membrane was immersed into 5 M HNO_3 to dissolve away all of the Ag. This left the Au microcylinders imbedded in the Anopore membrane (Figure 2C).

Figure 3 shows an electron micrograph of the Ag microcylinders obtained after depositing Ag into the pores. This micrograph was acquired by dissolving away the Anopore membrane in 1 M NaOH; note the high

microcylinder density. This micrograph also shows that the microcylinders obtained via this method are of uniform size and shape. Electron micrographs obtained after dissolution of the Ag indicate that the Au microcylinders are 300 nm in length and that all of the pores in the membrane contain microcylinders.

Fourier transform infrared spectroscopy (FTIR) was used to investigate the optical properties of the Au/Anopore composite membranes. The optical properties of a thin (300 nm) homogeneous Au film (electrochemically deposited onto the surface of an Anopore membrane) were also investigated. This thin homogeneous Au film served as a control.

The Ag plating solution is described in reference (5). The Au plating solution was obtained commercially (Orotemp 24, Technic, Inc.). An EG&G Model 173 Potentiostat/Galvanostat with a Model 179 digital coulometer was used to fabricate the Au/Anopore composite membranes. FTIR data was obtained with an IBM Model 44 spectrometer. Electron micrographs were obtained with a JEOL JSM 25SII scanning electron microscope.

RESULTS AND DISCUSSION

The Au microcylinders should be transparent to light which has wavelengths much greater than the diameters of the cylinders (3). Thus, infrared light was used to probe the optical properties of the Au/Anopore membranes. Figure 4A shows the FTIR spectrum of the Au/Anopore composite vs. a reference of virgin Anopore. The transmittance of the composite increases from 10 percent to 75 percent as the wavelength increases from 2.5 to 6.0 μm. The transmittance remains constant at 75 percent over the region 6.0 to 8.0 μm. The Anopore membrane itself absorbs strongly at wavelengths greater than 8 μm (Figure 4B). The raw transmittance data for the

Au/Anopore composite (i.e. not corrected for Anopore absorption) is shown in Figure 4C.

As noted above, Anopore membrane is ca. 65 percent pore space. If the Au particles were opaque, only 35 percent of the incident light would be transmitted through the Au/Anopore membrane. That 75 percent of the incident light is transmitted at wavelengths substantially greater than the diameter of the particles indicates that the transparency, predicted by effective medium theory, is observed. This conclusion was further confirmed by investigating the transmittance of a 300 nm-thick homogeneous Au film. This homogeneous film showed zero transmittance over the same wavelength region.

CONCLUSIONS

It is of interest to compare the results obtained here with results obtained by Heller et al. (2,3). Because Heller's synthetic method did not yield the optimal microstructure (3), high transparency was observed for films which were less than 50 nm in thickness. We have obtained good transparency for metal microstructures which are 300 nm thick. However, Heller's particles were sufficiently small that transparency in the visible region of the spectrum was achieved; where as, our larger particles are transparent in the infrared. We are currently attempting to synthesize Anopore-type membranes with smaller pores (6) so that metal microcylinders which are transparent to visible light can be obtained.

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FIGURE CAPTIONS

Figure 1 - Electrochemical Cell. A. Anopore membrane working electrode; B. Glass plate; C. O-ring seal; D. Pt counter electrode; E. Ag/AgCl reference electrode; F. Glass Cell; G. Plating solution; H. Stir bar.

Figure 2 - Fabrication of Transparent Metal Films. A. Deposition of silver; B. Deposition of gold into the pores; C. Dissolution of silver.

Figure 3 - Electron micrograph of Ag microcylinders.

Figure 4 - A. FTIR spectrum of Au/Anopore composite vs. reference of virgin Anopore; B. FTIR of virgin Anopore; C. FTIR of Au/Anopore composite uncorrected for absorbance of Anopore.

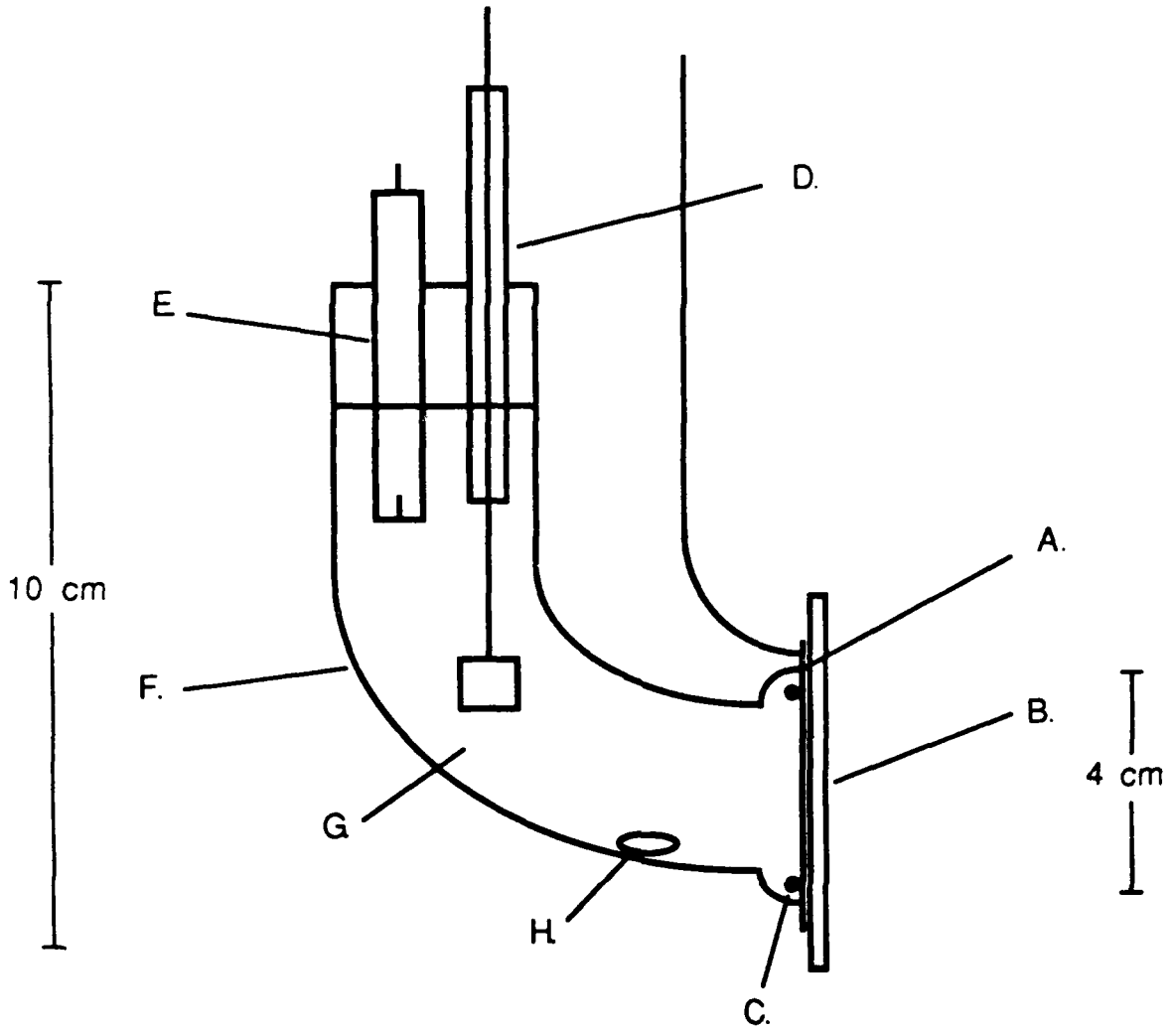

Fig 1

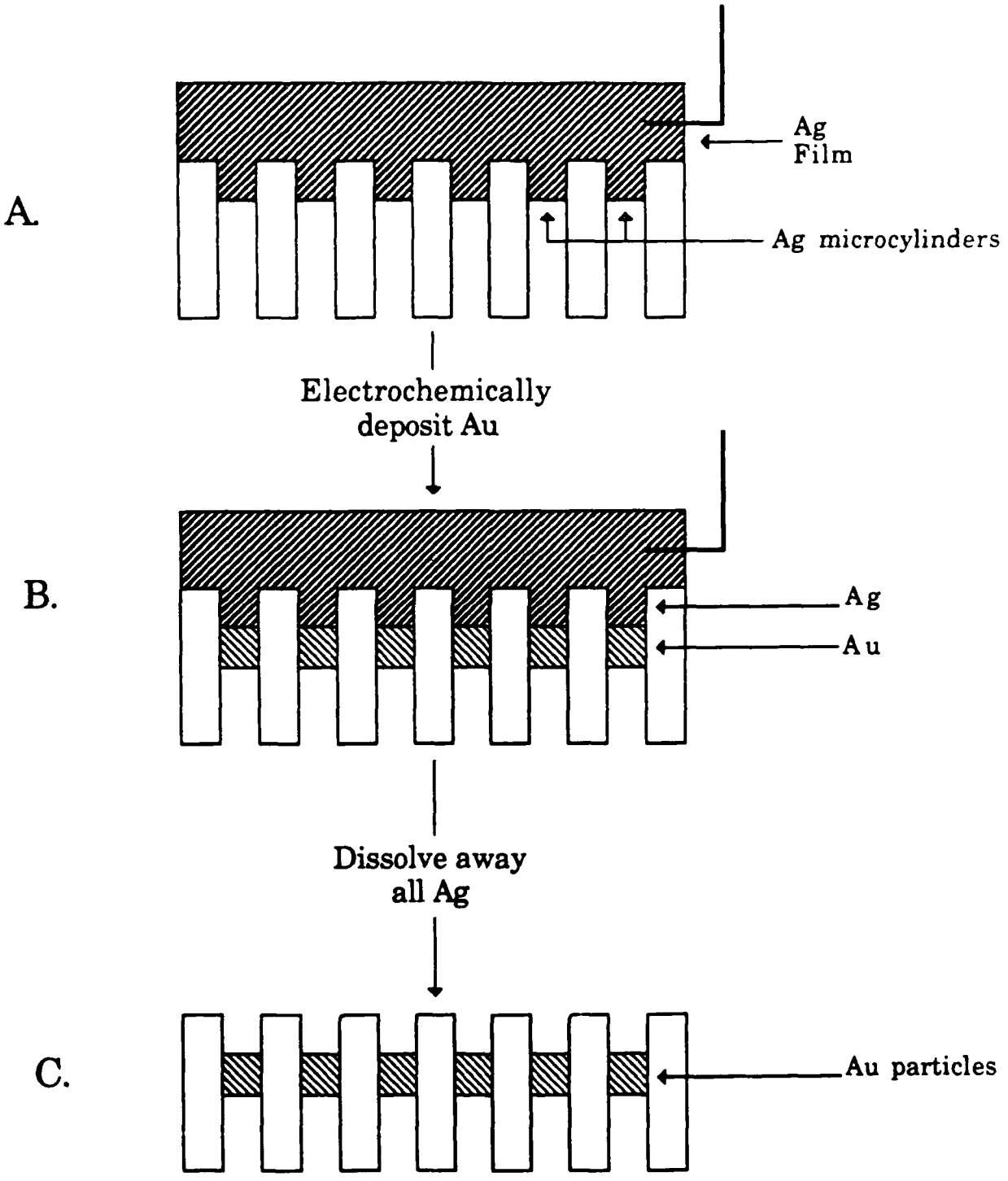
A.
Ag
Film
Ag microcylinders
Electrochemically
deposit Au
B.
Ag
Au
Dissolve away
all Ag
C.
Au particles

Fig 2

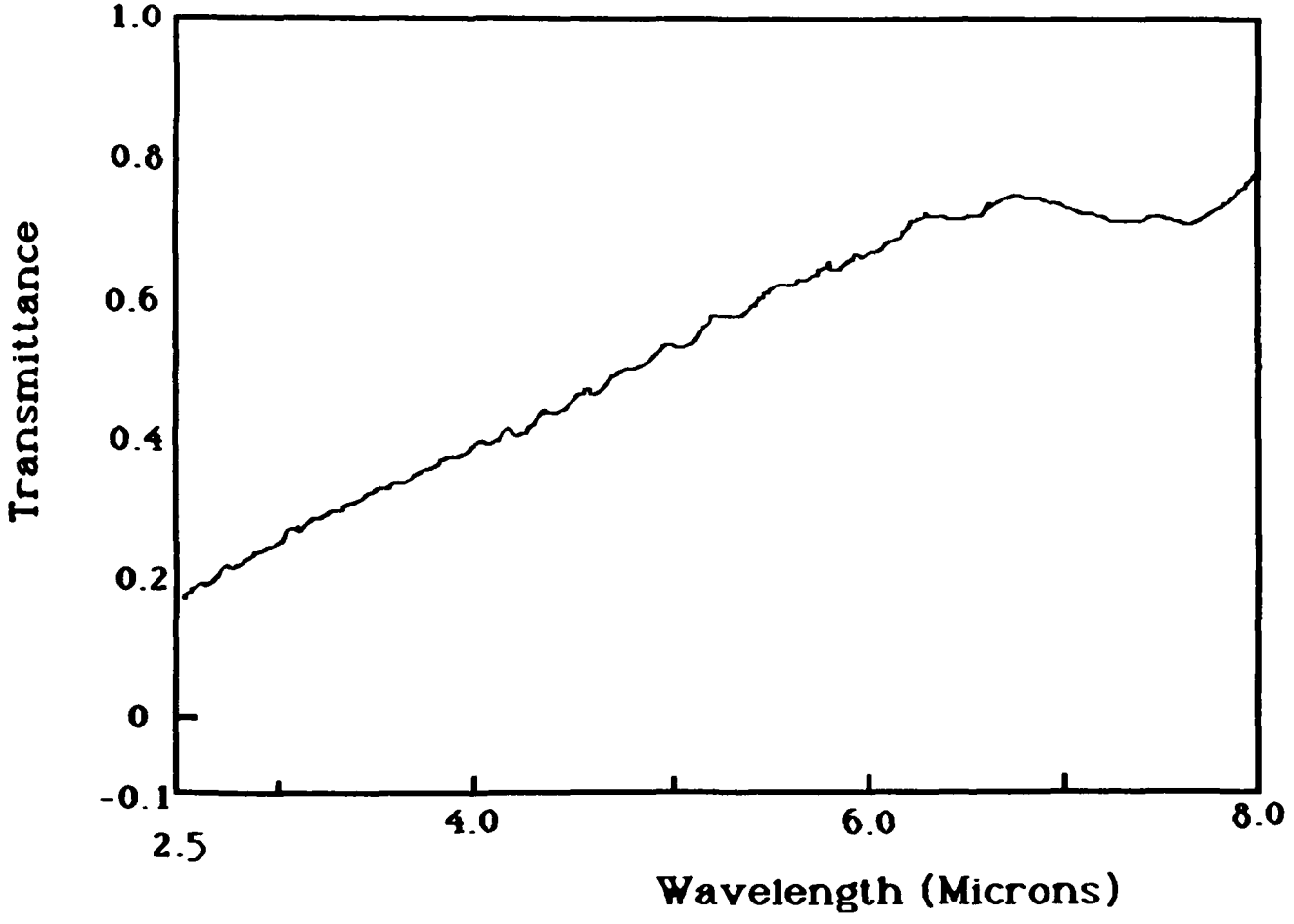
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Fig 4A

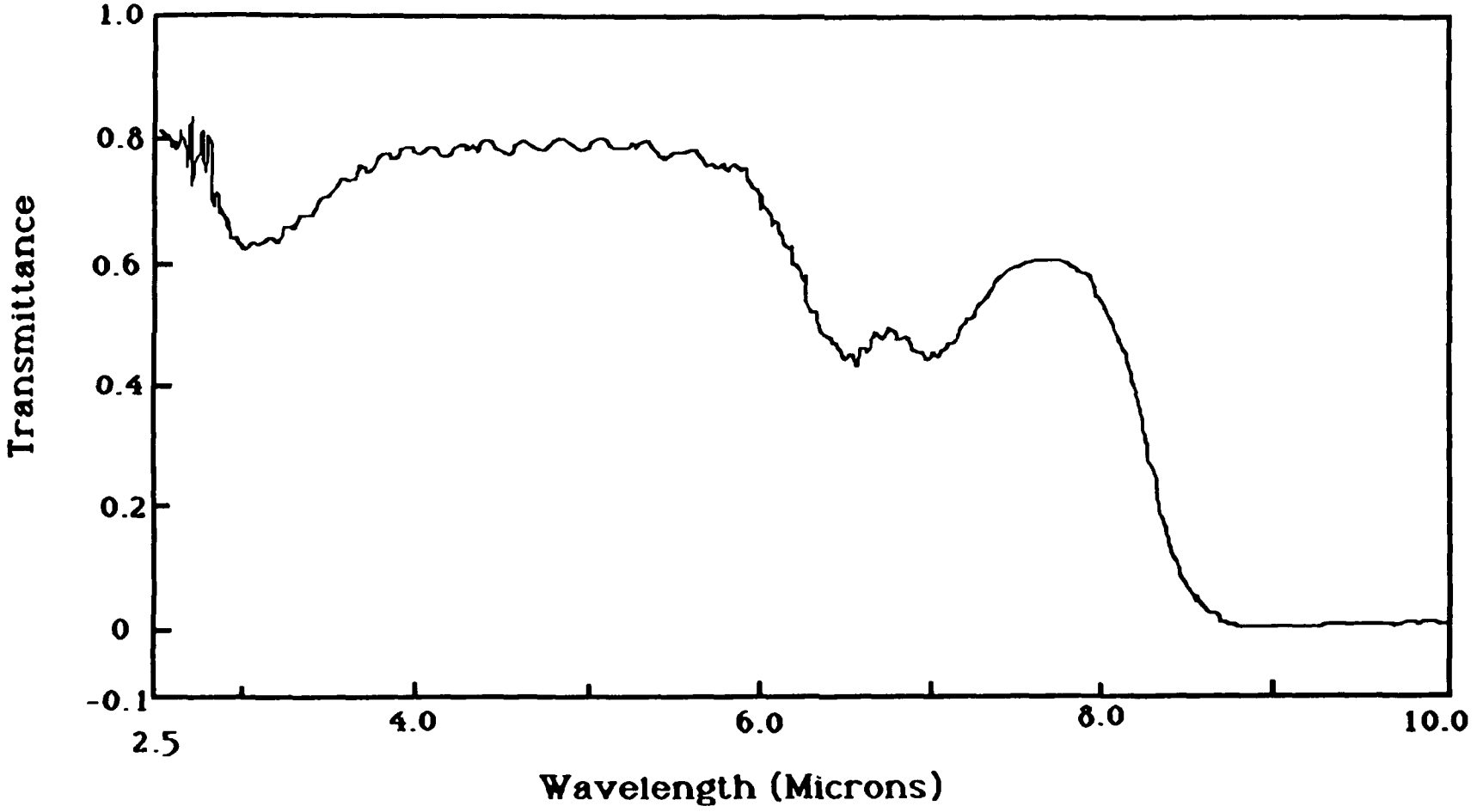
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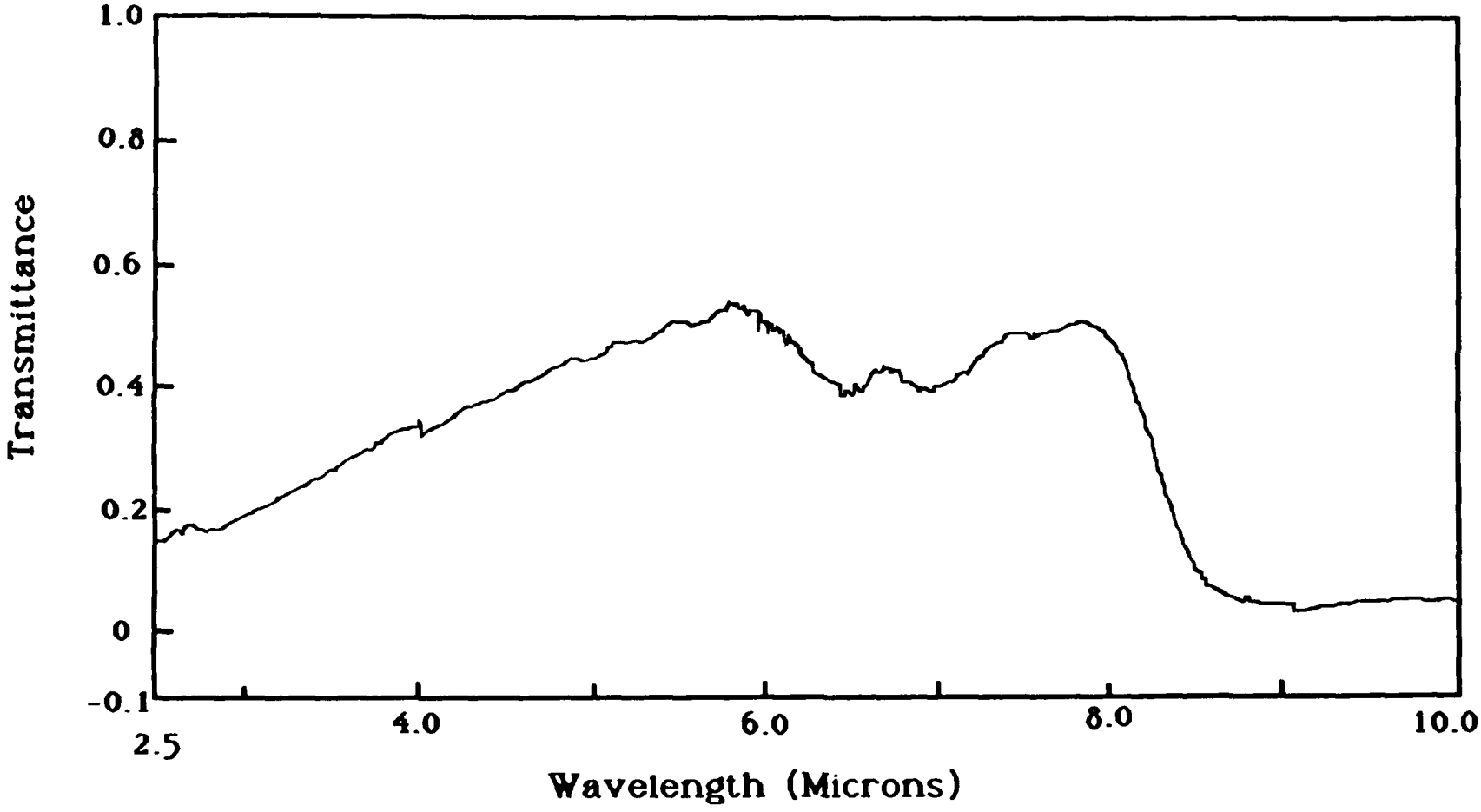
Fig 4B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Wavelength (Microns)

Fig 4C

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