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13. ABSTRACT *(Maximum 200 words)*
Nano-chemistry, physics and materials are important and evolving fields in modern science. One of the most interesting aspects of nanomaterials concerns the optical properties of nanoscopic metal particles. While bulk metals are optically opaque, effective medium theory (EMT) predicts that collections of small metal particles can be transparent, provided that the wavelength of light employed is much greater than a characteristic dimension of the particle. Hence, EMT can be used as a guide to prepare metal-containing composites that are both electronically conductive and optically transparent. We have recently shown that composites of this type can be prepared by electrochemical deposition of metals within the pores of a microporous "template" membrane. In this report we show for the first time that composite membranes prepared via this "template" route can be optically transparent throughout the near infrared (NIR) and into the visible region of the electromagnetic spectrum. Furthermore, we show that by changing the shapes of the particles prepared, the color of the composite membrane can be reproducibly and predictably varied. Finally, we show that these results are in general agreement with the predictions of the appropriate formulation of EMT.

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Optical Properties of Composite Membranes Containing Arrays of Nanoscopic Gold Cylinders

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ABSTRACT

Arrays of nanoscopic Au cylinders were prepared by electrochemical deposition of Au within the pores of nanoporous (pore diameter = 50 nm) alumina template membranes. We show, for the first time, that the Au/alumina composite membranes obtained can be optically transparent into the visible portion of the electromagnetic spectrum. We also show that by changing the aspect ratio of the Au nanocylinders prepared, the color of the composite membrane can be reproducibly and predictably varied. Finally, we show that these results are in agreement with the predictions of Maxwell-Garnett theory for metal-insulator composites.

Nano- chemistry [1], physics [2] and materials [3] are important and evolving fields in modern science. One of the most interesting aspects of nanomaterials concerns the optical properties of nanoscopic metal particles. While bulk metals are optically opaque, effective medium theory (EMT) [4] predicts that collections of small metal particles can be transparent, provided that the wavelength of light employed is much greater than a characteristic dimension of the particle [4]. Hence, EMT can be used as a guide to prepare metal-containing composites that are both electronically conductive and optically transparent [5-8]. Such composites are inherently interesting from a purely scientific viewpoint and have a variety of possible technological applications [7].

We have recently shown that composites of this type can be prepared by electrochemical deposition of metals within the pores of a microporous "template" membrane [8]. However, the metal particles investigated in our prior work were large (of diameters greater than 200 nm). As a result, the composite membranes were transparent in the infrared (IR) portion of the electromagnetic spectrum but opaque in the near IR (NIR) and visible regions. Our goal, since publishing this work [8] has been to push this optical transparency into the visible portion of the spectrum. In order to accomplish this objective we synthesized alumina template membranes [9,10] with much smaller pore diameters than the membranes used in our previous work. We also modified the electrochemical methods used to deposit the metal particles in these "nanoporous" alumina membranes [10].

In this report we show for the first time that the Au/alumina composites obtained by depositing Au into these nanoporous template membranes can be optically transparent throughout the NIR and into the visible region of the electromagnetic spectrum. Furthermore, we show for the first time that by changing the shapes of the particles prepared, the color of the composite membrane can be reproducibly and predictably varied. Finally, we show that these results are in agreement with the predictions of the appropriate formulation of EMT.

The alumina template membranes were prepared electrochemically from Al metal [9,10]. The details of the membrane syntheses will be given in [10]. These membranes contain cylindrical pores of uniform diameter [8-10]. Membranes with pore diameters of 50 nm were prepared for these studies. A transmission electron micrograph (TEM) of a typical membrane is shown in Figure 1A; the pore diameters were evaluated from such micrographs. Au microcylinders were deposited within the pores using a modified form [10] of the electrochemical method described in our previous work [8]. The diameters of these cylinders is determined by the diameter of the pores in the membrane; the aspect ratio is determined by the quantity of metal deposited. Figure 1B shows a TEM of a cross section of a template membrane after deposition of the Au microcylinders. In this case the cylinders are 50 nm in diameter and 500 nm in length (aspect ratio = 10). A related electrochemical method has been used to prepare composites for selective absorption of solar energy [11]. However, particles with known aspect ratios could not be obtained via this earlier method [11].

The ability to reproducibly and predictably control both the diameter and aspect ratio of the metal microcylinders prepared is an important feature of the template method. Furthermore, the template method yields metal particles which are completely isolated from each other, with uniform lateral separation distances. Finally, the template synthesized metal particles are oriented in the same direction in space (Figure 1B). As we shall see, all of these features are critical in determining the optical properties of these Au/alumina composite membranes.

Figure 2 shows a transmittance spectrum of a composite containing Au cylinders that are 50 nm in diameter and approximately 50 nm in length (aspect ratio = 1). This composite is substantially transparent throughout the NIR and into the visible portion of the spectrum. This is the first time that transparency to such short wavelengths of light has been demonstrated for template-synthesized metal particles. Note further that a strong absorption band is observed near the plasma frequency of Au [12].

Figure 3 shows a close-up of the plasma band for composites containing Au particles with two different aspect ratios - for Curve A the particles are 50 nm in diameter and 50 nm in length; for Curve B the particles are also 50 nm in diameter, but are ca. 300 nm in length. The plasma band for the long narrow cylinders is blue-shifted relative to the plasma band for the cylinders with an aspect ratio of unity. As a result, **the color of the composite varies with the shape of the Au particles within the membrane.** The membrane corresponding to Curve A transmits a blue-purple color; the membrane corresponding to Curve B is deep red in color. While this affect of particle aspect ratio on optical properties has been treated theoretically [11], to our knowledge, this is the first time that this aspect ratio-color dependence has been demonstrated experimentally.

All of these observations - the high optical transparency, the strong plasma absorption and, most importantly, the change in color with particle shape - are predicted by the Maxwell-Garnett (M-G) formulation of EMT [4]. According to M-G theory, the dielectric function of the composite membrane, ε, containing nanoscopic metal particles is related to the dielectric functions of the metal, ε_m, and the host membrane, ε_o, via [4]

$$\frac{\varepsilon - \varepsilon_o}{\varepsilon + \kappa\varepsilon_o} = f_m \frac{\varepsilon_m - \varepsilon_o}{\varepsilon_m + \kappa\varepsilon_o} \qquad (1)$$

where f_m is the volume fraction occupied by the metal particles and κ is a "screening" parameter that depends on the shape of the particles [4,5]. Spherical particles have $\kappa = 2$, whereas long, needle-like particles aligned with their principal axes parallel to the direction of light incidence have $\kappa = 1$ [5]; these values of κ are of interest to the work described here because the Au particles with aspect ratio = 10 approach the long, needle-like limiting case, and the particles with an aspect ratio of unity can be treated as spheres.

Equation 1 can be used to simulate absorption spectra for our Au/alumina composites. Figure 4 shows simulated absorption spectra for composites containing spherical (Curve A) and needle-like (Curve B) particles. In agreement with the experimental observations (Figures 2 and 3), these simulated spectra show that the composites are highly transparent at energies below the plasma absorption band. Furthermore, the plasma absorption maximum for the needle-like particles ($\kappa = 1.2$) is blue shifted relative to the maximum for spherical particles ($\kappa = 2$). Hence, this simple theoretical analysis explains the experimentally-observed change in color of the composite membranes with the shape of the Au particles.

The template method allows for precise control over size, shape and orientation of metallic (and polymeric [13]) particles produced within the porous membrane. We are especially interested in preparing particles with even smaller diameters because the extent of transparency to visible light should be further improved. We are also investigating applications of such arrays of small metal particles in surface enhanced absorption and Raman spectroscopies, chemical catalysis, and chemical sensors.

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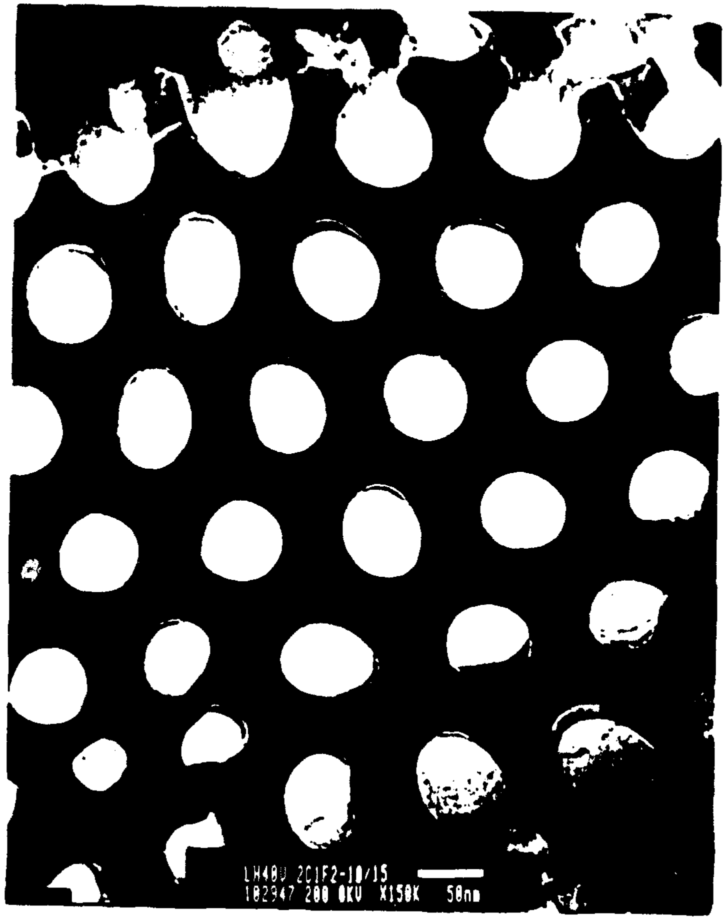
Figure Captions:

Figure 1. A) Transmission electron micrograph of porous alumina membrane prepared in 2% oxalic acid at 40 V. Scale bar = 50 nm. B) Transmission electron micrograph of a cross-section of an alumina memebrane after deposition of the Au nanocylinders. The cylinders are dispersed in a layer ca. 1 μm from the top face of the membrane (top of micrograph) Arrow points to nanocylinder layer. Scale bar = 1 μm.

Figure 2. Transmission spectrum of alumina membrane before deposition of Au particles (Curve A) and Au/alumina composite membrane containing sphere-like Au particles 50 nm in diameter (Curve B).

Figure 3. Absorption spectrum of Au/alumina composite membranes. Curve A: particle diameter = 50 nm, particle length = 50 nm. Curve B: particle diameter = 50 nm, particle length = 300 nm.

Figure 4. Simulated absorption spectra based on equation 1 and Au optical properties from reference 7. Curve A: $\kappa = 2$, $f_m = 0.05$, path length = 0.3 μm. Curve B: $\kappa = 1.2$, $f_m = 0.15$, path length = 0.48 μm.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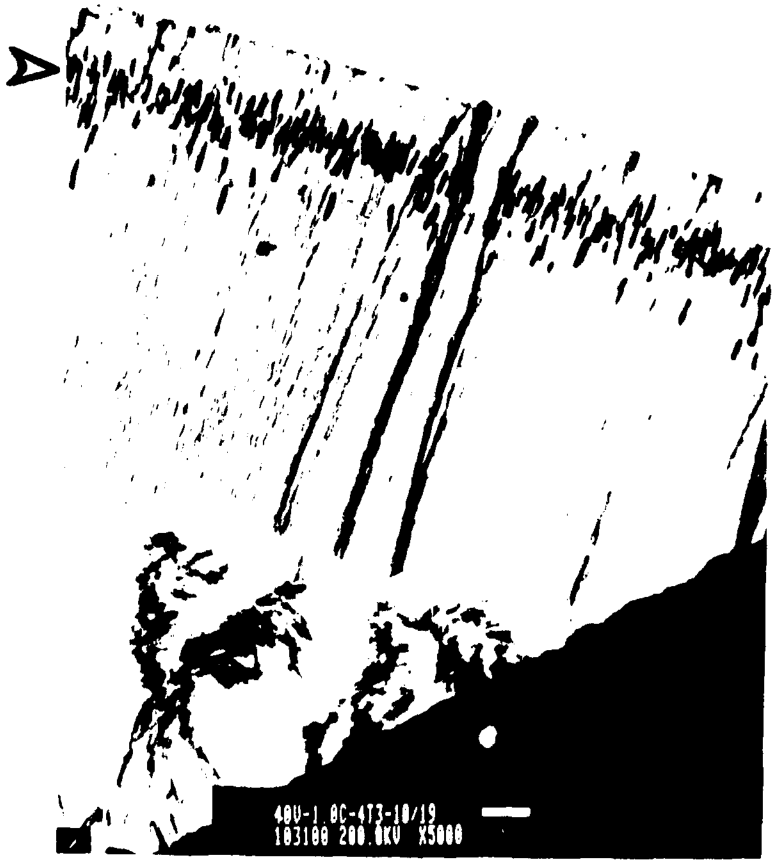
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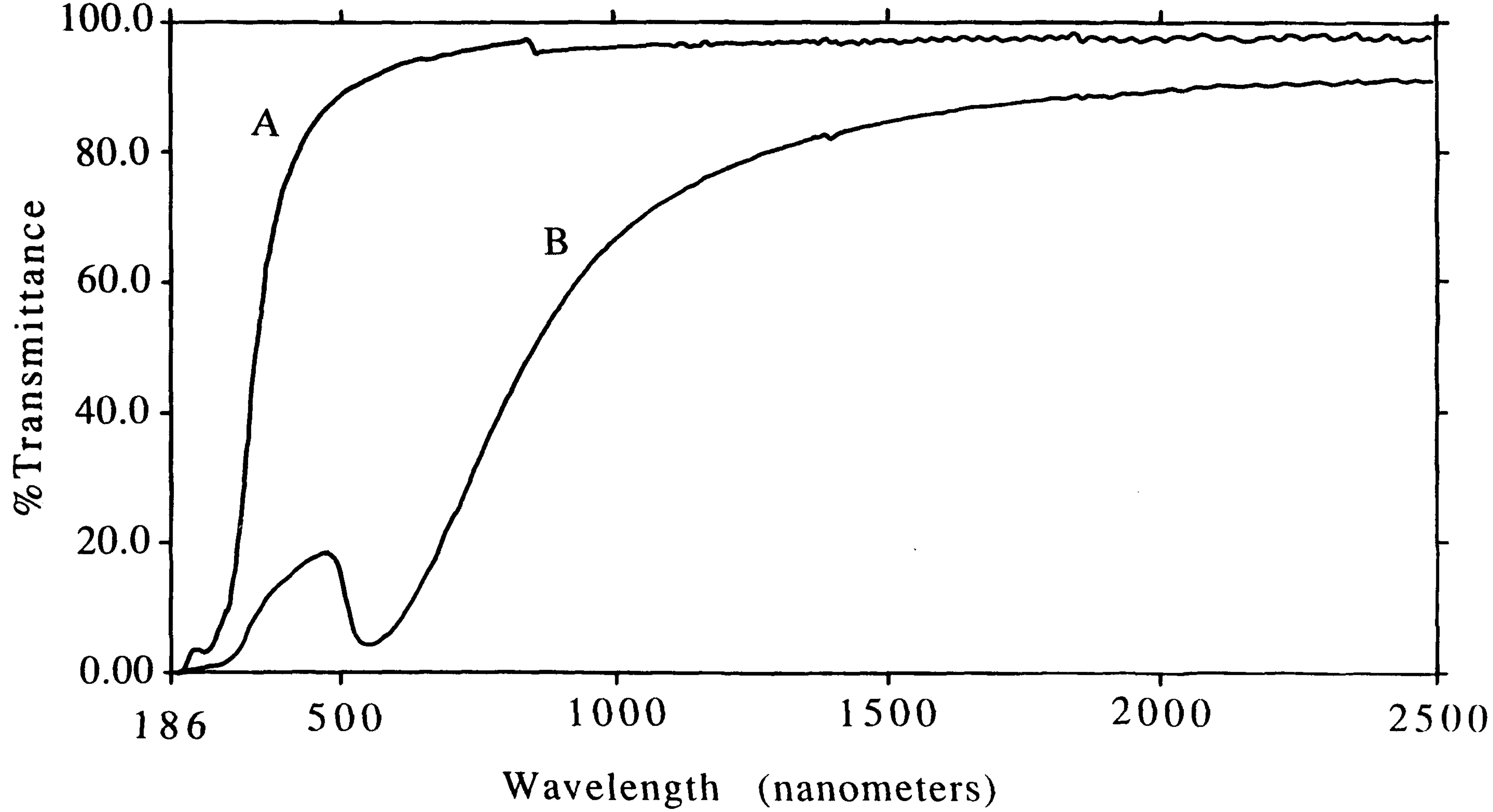
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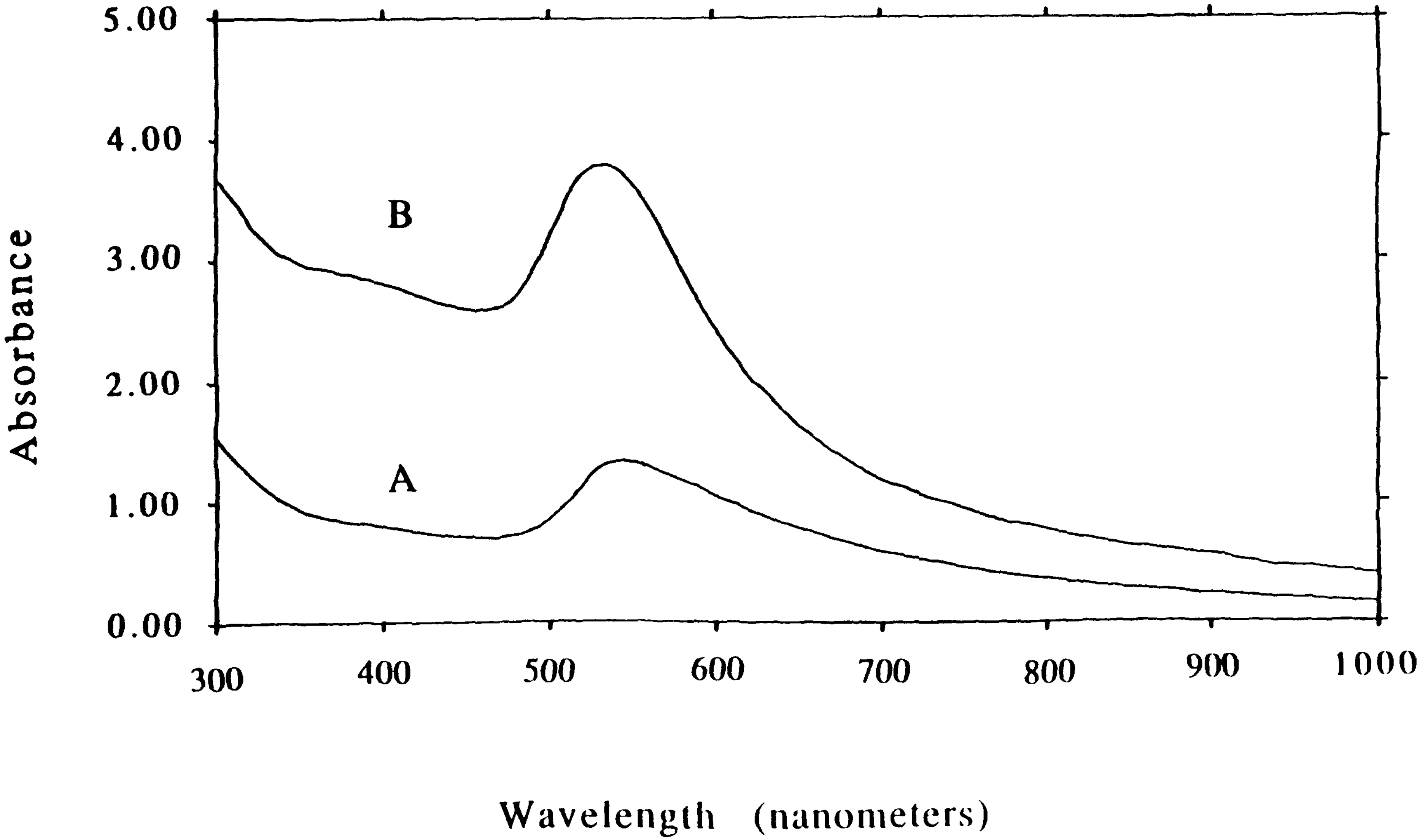
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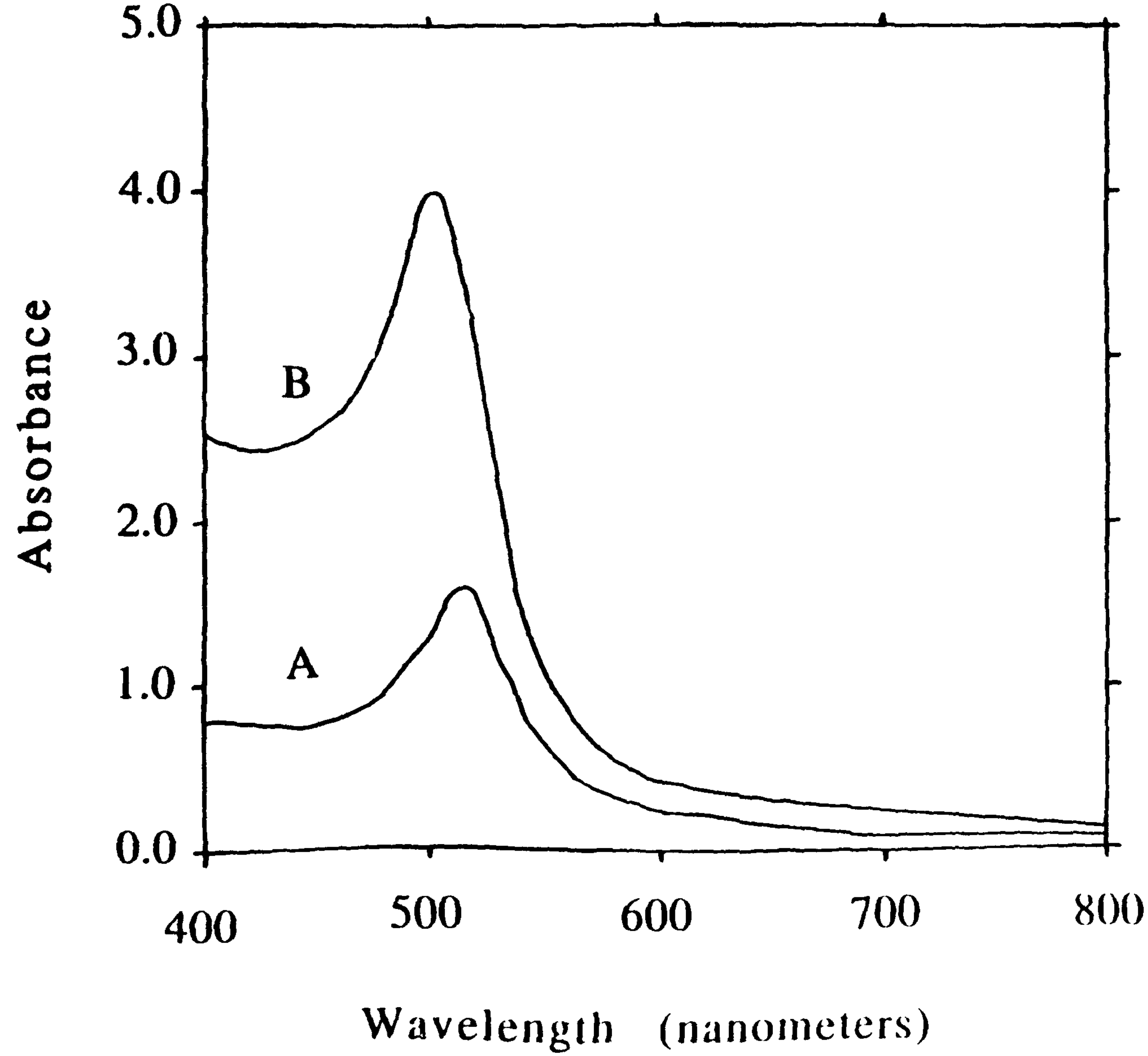

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