

NOVEL ELECTROLESS TEMPLATE BASED SYNTHESIS OF SILVER MICROTUBULES AND THEIR CHARACTERIZATION

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This paper describes novel electroless method for synthesis of silver microtubules via use of track etch membrane as template. Silver microtubules were characterized by scanning electron microscope (SEM) and UV-visible spectrophotometer. The SEM characterization shows the formation of freestanding hollow silver microtubes even after the deposition is carried out for longer time (e.g. 48 hrs). The slight shift in surface plasmon resonance absorption peaks in silver microtubes with increasing deposition time is observed through UV-visible spectrophotometric measurements.

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1. Introduction

Nano-micro structures with hollow interiors have attracted attention for their potential applications in drug delivery systems, microelectronics, enzyme bio-reactors, chemical and biochemical sensing devices [1-3] etc. The introduction of surface plasmon resonance (SPR) phenomenon occurring at metal surfaces (typically silver and gold) in the early 1990s, made use of hollow structures of metal or carbon nanotubes decorated with gold and silver as catalysts. Other applications include broad band optical limiters, electrodes, advanced materials and optical switching applications [4-8]. Many methods such as electrochemical deposition, sol-gel, chemical vapour deposition (CVD), chemical polymerization, electroless plating etc. have been used for fabrication of such structures [9-12]. In this paper, we report a novel synthesis route for the fabrication of arrays of silver tubules via electroless deposition using track etch membranes as templates. Electroless method was firstly reported by Brenner and Riddell [13] for deposition of cobalt and nickel thin films and generally involves two mechanisms: galvanic displacement and autocatalytic. Galvanic displacement depends upon the relative position in electrochemical cells whereas autocatalytic requires the presence of a catalyst. Palladium (Pd) and Platinum (Pt) are good choices as catalyst.

Template based synthesis makes use of a template membrane that contains large number of micro or nano pores. Generally, two types of membranes i. e. track etch membranes and anodic alumina oxide (AAO) membranes are used. In our case, we have used track etch membranes as templates for synthesis of Ag microtubules. Production of track etch membranes involves energetic heavy-ion irradiation of a suitable polymer foil which results into generation of latent tracks, followed by chemical etching of latent tracks. Ion irradiation of a polymer foil causes damage tracks in it. These damaged tracks can be chemically etched using suitable etchants [14] and result into the formation of pores of controlled size in it. Track etch membranes are also commercially available from Whatman, Nuclepore, Poretics, Millipore [15] etc.

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2. Materials and methods

Formation of track etch membrane.

Makrofol polycarbonate foils of thickness 10 μ m were irradiated with normally incident Si⁸⁺ having energy 10 MeV at GPSC of Inter University Accelerator Center, New Delhi, India. The fluence was of the order of $2 \times 10^5/\text{cm}^2$. The energy of ion was so chosen that projectile range was greater than the thickness of the foil and energy loss was well above the threshold required for homogeneous etching. The irradiated foils were chemically etched in 6N NaOH solution at 55 °C for 1h 50 min resulting into the formation of pores of the order of 2 μ m in it.

Sensitization and activation of membrane.

The track etch membrane was pre-activated and activated at room temperature (25 °C) using 10g/l SnCl₂ and 10ml/l HCl (37%); 0.1g/l PdCl₂ and 10ml/l HCl (37 %) solutions for 2 h and 15 min., respectively. The surface of the membrane was deactivated by rubbing it with cotton using water/methanol solution so that the deposition started along the pore walls rather than onto the surface which might act as hindrance to autocatalytic growth through the pores.

Silver (Ag) deposition

The activated membrane was dipped in freshly prepared silver-plating solution, which was prepared by mixing two solutions contained in baths 1 and 2. Bath 1 contained 2.3 g AgNO₃, 2ml liquid ammonia and 25ml distilled water. Bath 2 contained 8g KNaC₄H₄O₆ 4H₂O, 0.6g CoSO₄ and 25 ml distilled water. The two solutions were mixed and diluted 7 times with distilled water. The electroless plating was done for 2hr, 24 hr and 48 hr at 40 °C constant temperature. After the deposition was over, the membrane was thoroughly rinsed with 1:1 water methanol solution and dissolved in CH₂Cl₂ solvent for further analysis.

The deposition was confirmed by measuring the resistance across the filled pores, which came out to be of the order of only a few ohms indicating the Ag deposition.

Characterization.

The rinsed and dried samples were mounted on specially designed aluminum stub with the help of double adhesive tape, coated with layer of gold-palladium alloy in "JEOL", FINE SPUTTER JFC1100" sputter coater and viewed under the scanning electron microscope (SEM, JEOL, JSM6100) at an accelerating voltage of 20 KV. The UV-visible absorption spectra of silver tubules embedded within the track etch membrane were measured on Sizamu UV2525 spectrophotometer. Track etch membrane is good transparent template for investigating the optical properties of silver tubules because of its weak absorption.

3. Result and discussion

The sensitization of pore walls of track etch membrane with Sn²⁺ sensitizer binds Sn²⁺ to the surface of the pore walls. The activation with Pd²⁺, results into the formation of Sn/Pd colloidal on the pore walls and surface of the membrane. This activated membrane when immersed in silver-plating solution leads the chemically reduced pore walls causing reaction and reduction of Ag metal from the plating solution.

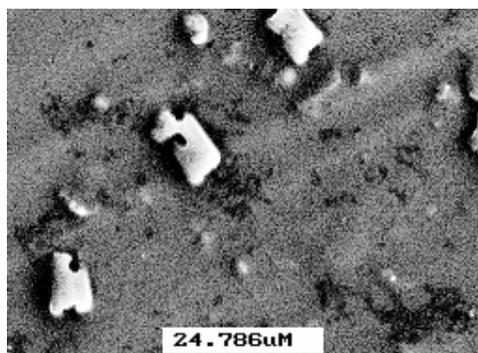


Fig.1. SEM photograph of silver microtubules (plating time 2 h).

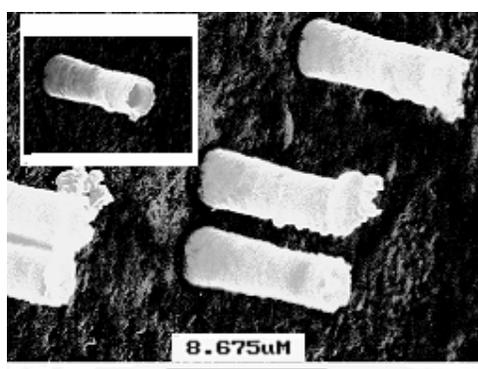


Fig. 2. SEM photograph of silver microtubules (plating time 24 h) with closer view(inset).

Figs. 1, 2 and 3 show the SEM photographs of silver tubules for different deposition times viz 2 h, 24 h, and 48 h, respectively. For 2 h plating the thickness of the tubes was so small that these could not withstand and turned into debris when released from the template (Fig.1). However, when deposition was carried out for 24 h, the thickness of the tubes became sufficient so that freestanding tubes were obtained. The inner diameter of the hollow tubules can be controlled by adjusting the deposition time. The thickness of walls of microtubules appears to be increased when deposition is carried out for 48 h indicating that deposition rate is much slower due to weak catalytic action of silver. This is because initial reaction is fast but once Pd ions are used up silver itself acts as catalyst (although much less active than palladium) to sustain the reaction and deposition continues at slower rate after a certain thickness is reached e.g., a few hundreds of nanometers, which results into the formation of hollow silver microtubules rather than solid rods like structures even after the plating is done for longer time 48 h (Fig.3).

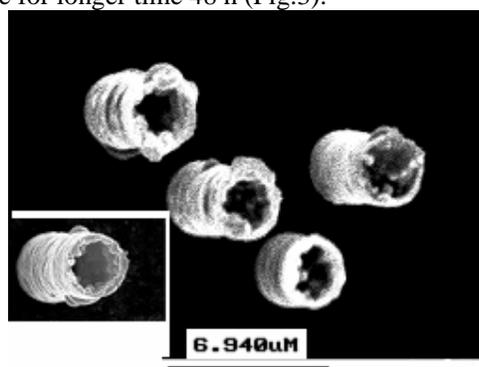


Fig.3. SEM photograph of silver microtubules (plating time 48 h) with closer view (inset) showing the formation of hollow tubules.

The fundamental optical property of silver microtubes investigated here is the absorption using UV-visible spectrophotometer. Figure 4 shows the absorption spectra of track etch membrane and silver microtubes embedded in track etch membrane, respectively. The absorption spectrum of Ag microtubes shows wider peak with increased deposition time besides slight shift in peak to decreased wavelength with increased deposition time. The absence of absorption peak in track etch membrane (Fig.4) confirms the absorption shown by Ag structures.

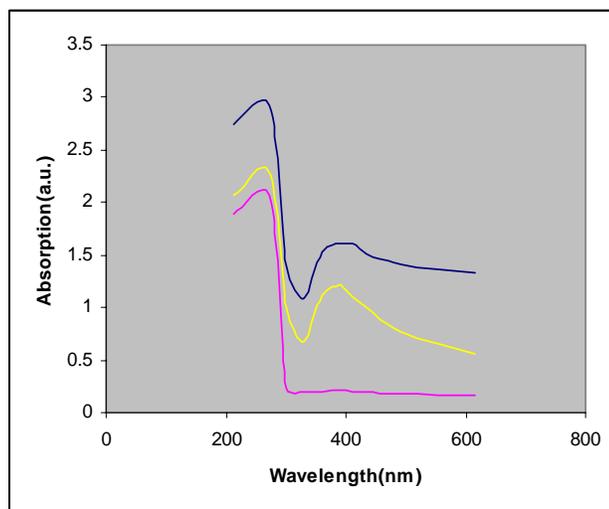


Fig. 4. UV-visible absorption spectrum of (a)Makrofol (polycarbonate) track etch membrane (b)silver microtubules embedded in Makrofol membrane (plating time 24 h) (c) Silver microtubules embedded in Makrofol membrane(plating time 48 h).

This absorption band is attributed to quantum optical-electrical phenomenon known as Surface plasmon resonance (SPR) arising from the interaction of light with a metal surface. It is well known that under certain conditions the energy carried by photon of light is transferred to packets of electrons, called plasmons, on a metal surface. This energy transfer occurs only at a specific resonance wavelength of light i.e. the wavelength where the quantum energy carried by photons exactly equals the quantum energy levels of the plasmons. Surface plasmon resonance acts as basis for sensor technology, optical limiting and potential optical switching applications, advanced materials etc.

This method is simple and can be easily used for coating inner pore walls in track etch membranes, glass membranes and tubes etc. It can be helpful in fabricating electronic, optical and analytical devices such as capillaries for high-resolution NMR spectroscopy, microsprings, fibre gratings, intravascular stents [16-18] etc.

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