



## APPLICATION OF TEMPLATE-BASED POLYANILINE NANOTUBES SYNTHESIZED IN ANODIC POROUS ALUMINA

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*Received November 24, 2009*

An anodic aluminum oxide template-based process was adopted to fabricate polyaniline (PANI) nanotubes using the electropolymerization process. In addition, copper nanowires were synthesized into the PANI nanotubes by the "second-order-template" method. Cyclic voltammetry, potentiostatic and galvanostatic methods were performed for the fabrication of the nanostructures. The effect of the polymerization bath composition on morphology of nanotubes has been studied by means of scanning electron microscopy (SEM). Studies regarding the morphology of the polyaniline nanotubes filled with copper were performed, as well as the elemental analysis by energy dispersive X-ray spectroscopy (EDAX).

### INTRODUCTION

Due to owing to their high surface-to-volume ratio, unique property to accelerate electron transfer and high surface free energy, the nanostructured conducting polymers (NCPs), have recently received much interest.<sup>1-2</sup> Among various NCPs, polyaniline (PANI) is one of the more important conducting polymers due to its relatively easy processability, electrical conductivity and environmental stability.<sup>3,4</sup> Polyaniline is unique among conducting polymers in that its electrical properties can be reversibly controlled by both charge-transfer doping and protonation. Nanostructured PANI has potential applications in biosensors, actuators, drug delivery systems, gas sensors, etc.<sup>5-8</sup>

Nanostructured PANI, with different morphologies, has been synthesized using various techniques such as template synthesis, self-assembly, emulsions and interfacial polymerization.<sup>9-12</sup> Polyaniline nanowires and nanotubes have been synthesized using a solid template, such as porous membrane.<sup>13</sup>

The means of controlling their morphology without the use of templates are so far rather limited. The advantage of the typical template synthesis is the simplicity of the control of nanotube diameter, length and orientation.<sup>14</sup> By using the template-based synthesis method, unique and ordered nanostructures can be built. Recently, metal-filled PANI nanotubes have attracted some attention due to their interesting properties, such as the magnetic ones.<sup>15</sup>

In this paper, we describe a systematic study of the electrochemical growth of polyaniline from aqueous H<sub>2</sub>SO<sub>4</sub> solutions in anodic aluminum oxide (AAO) membranes, and the effect of different parameters on the morphology of the resulting nanotubes. An array of copper nanowires enveloped in polyaniline nanotubes was prepared by the "second-order-template" method. The properties of the obtained nanotubes were assessed.

Many studies have focused on the fabrication of copper nanowires, because of their potential applications in the micro/nanoelectronics industry and, in particular, for interconnection in electronic circuits.<sup>16-19</sup>

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## EXPERIMENTAL

All chemicals were of the highest quality commercially available: aniline (Aldrich, >99.5%), H<sub>2</sub>SO<sub>4</sub> (Wako Chemicals), CuSO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, HCl and NaCl (Aldrich). All chemicals were used as received.

Electrochemical experiments were carried out with PC-controlled AMEL 5000 instrument, in a one-compartment, three-electrode cell at room temperature, using a platinum net as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. All potential are measured with respect to the SCE. SEM images were obtained with FEI 50 scanning electron microscope.

Anodic aluminum oxide (AAO) membranes (Whatman) with the pore size of 200 nm and thickness of 60 μm were used as the templates for the polymerization of PANI nanotube arrays. The working electrode for the electropolymerization was achieved by depositing a 120 nm thick Au layer on the branched side of the template with a BOC Edwards magnetron sputter coater. The electrode (effective area 0.2 cm<sup>2</sup>) was placed in such a way that the monomer solution could access the working electrode only through the pores of the membrane. PANI was obtained by different electrochemical methods.

When the polymerization process was completed, the sample was removed and rinsed with the corresponding acid solution and Milli-Q water. In order to observe the

morphology of the nanotubes, the template was removed in 1M NaOH for 15 minutes and then the samples were repeatedly rinsed with deionized water to remove residual NaOH, followed by drying at 100°C for 30 minutes. After the PANI was electropolymerized in the pores of alumina, the deposition of copper nanowires into the PANI nanotubules was performed.

## RESULTS AND DISCUSSION

The template-based electropolymerization of aniline was performed by means of potentiostatic method, under a constant potential of 900 mV, by cyclic voltammetry sweeping the potential in the window -200mV to 950mV, at a scan rate of 20 mV s<sup>-1</sup> for 20 cycles, and by galvanostatic method under a constant current density of 5.5 mA cm<sup>-2</sup>.

The polymerization was conducted under varying concentrations of supporting electrolyte and monomer. The H<sub>2</sub>SO<sub>4</sub> concentration varied from 0.1M to 1M and the monomer concentration from 0.1 to 0.5M.

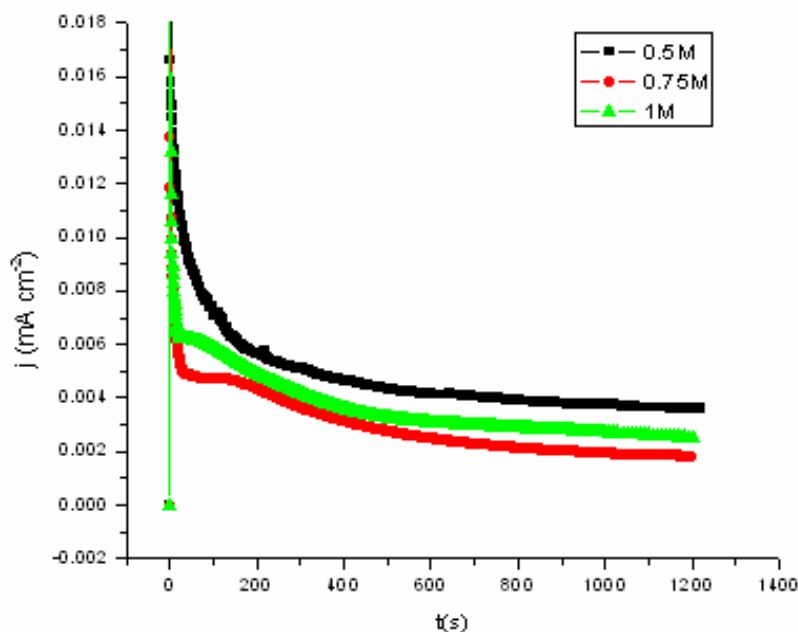


Fig. 1 – Current transients of aniline polymerization at different H<sub>2</sub>SO<sub>4</sub> concentrations. The monomer concentration was 0.1 M and the polymerization potential was 900 mV.

Figure 1 shows the current transients for a series of experiments in which the H<sub>2</sub>SO<sub>4</sub> concentration was varied. All the I-t curves follow the same trend. There is an initial current drop, which is typical of polyaniline electropolymerization. It has been attributed in different studies to charging current, oxidative

electroadsorption of monomers and substrate passivation.<sup>20-22</sup> Following the initial current drop, the current rises slowly to a maximum value before gradually falling again.

As it can be seen in figure 1, the current maximum shifts to a shorter time and higher current as the H<sub>2</sub>SO<sub>4</sub> concentration increases. This

can be explained by a faster diffusion rate of monomers to the electrode at higher  $\text{H}_2\text{SO}_4$  concentration. The increase in diffusion coefficient with increasing electrolyte concentration has been observed in other systems, and is possibly due to the modulation of the hydrodynamic radius of the diffusing species as the ionic strength changes.<sup>23-25</sup> Another effect of increased  $\text{H}_2\text{SO}_4$  concentration is the increased rate of hydrolysis of polyaniline under anodic conditions.<sup>26</sup>

In figure 2 there are presented some of the E-t curves recorded during galvanostatic polymerization at a constant current of  $5.5 \text{ mA cm}^{-2}$  in which monomer and  $\text{H}_2\text{SO}_4$  concentration were varied. It can be observed that the potential reaches the

maximum in shorter time, at a lower value and also the value of the plateau potential decreases as the  $\text{H}_2\text{SO}_4$  concentration increases and moreover as the monomer concentration increases as well.

Regarding the monomer concentration, it is known that Fick's first law states that the diffusion flux is proportional to the concentration gradient.<sup>27</sup> Indeed, we observed a transition in the potential transient behavior at higher monomer concentration, as shown in figure 2. At higher aniline concentration, the potential maximum is followed by a slow decrease. It is seen that, at lower aniline concentration and higher  $\text{H}_2\text{SO}_4$  concentration, the transient have a shape expected for 3D nucleation and growth under diffusion control.

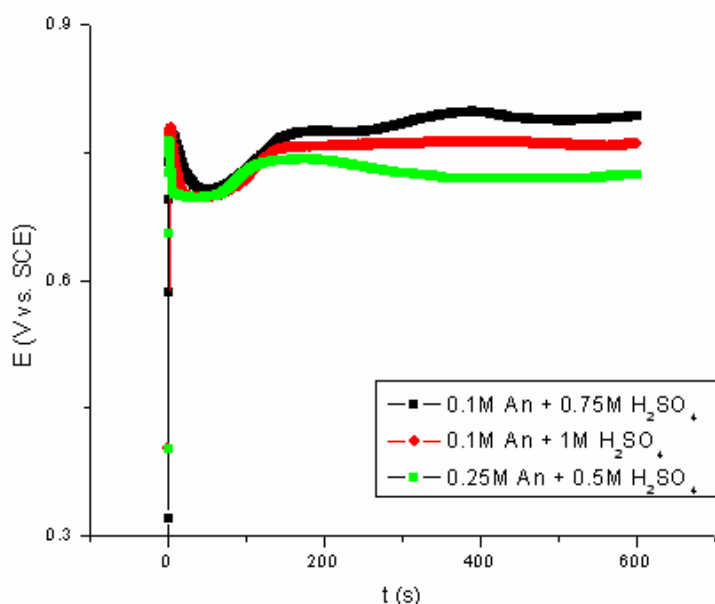


Fig. 2 – Galvanostatic polymerization of aniline at a current density of  $5.5 \text{ mA cm}^{-2}$  in different bath compositions.

Cyclic voltammetry was also employed for the study of the template-based electropolymerization of aniline. The cyclic voltammogram of 20 cycles shown in figure 3 illustrates the growth of polyaniline in the pores of alumina template at a scan rate of  $20 \text{ mV s}^{-1}$ . The first cycle shows the monomer oxidation at approximately  $0.9 \text{ V}$  in the forward scan, though the oxidation of aniline is not clearly seen in the forward scan of the first cycle, the reverse scan shows a small shoulder at  $0.45 \text{ V}$  and  $0.35 \text{ V}$ , which is due to the reduction of polyaniline formed on the electrode. The growth of the polyaniline upon cycling is reflected from the increase in current response as well as due to the well-defined peaks at  $0.2$  and  $0.48 \text{ V}$ , which are due to the oxidation of polyaniline formed on the electrode surface.

SEM images of the polyaniline synthesized from solution of  $0.1 \text{ M}$  monomer in  $0.5 \text{ M H}_2\text{SO}_4$  in the pores of the commercial alumina template of  $200 \text{ nm}$  in diameter are presented in figure 4 as a function of the electrolyte concentration and the polymerization method, after the template removal. It can be seen clearly the formation of nanotubes in figure 4b. The nanotubes surface in figure 4a is very smooth with homogenous diameter. From the SEM images, the average diameter is estimated to be  $230\text{--}260 \text{ nm}$  which is consistent with the pore size of the AAO template. The morphology of the nanotubes is highly homogenous and it shows that electrochemical process is effective in the deposition of polyaniline nanowires uniformly over the exposed area independent of the polymerization method.

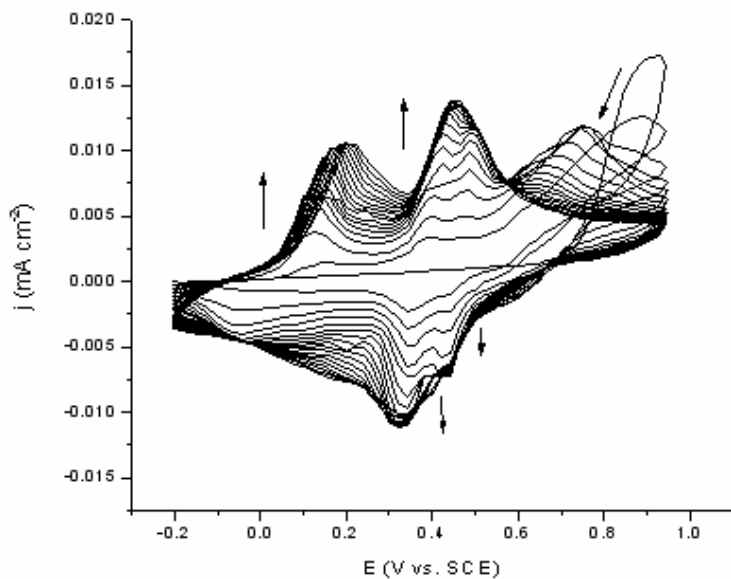


Fig. 3 – Electropolymerization of 0.1 M aniline in 1 M  $\text{H}_2\text{SO}_4$  in the alumina template by cyclic voltammetry. Scan rate  $20 \text{ mV s}^{-1}$ .

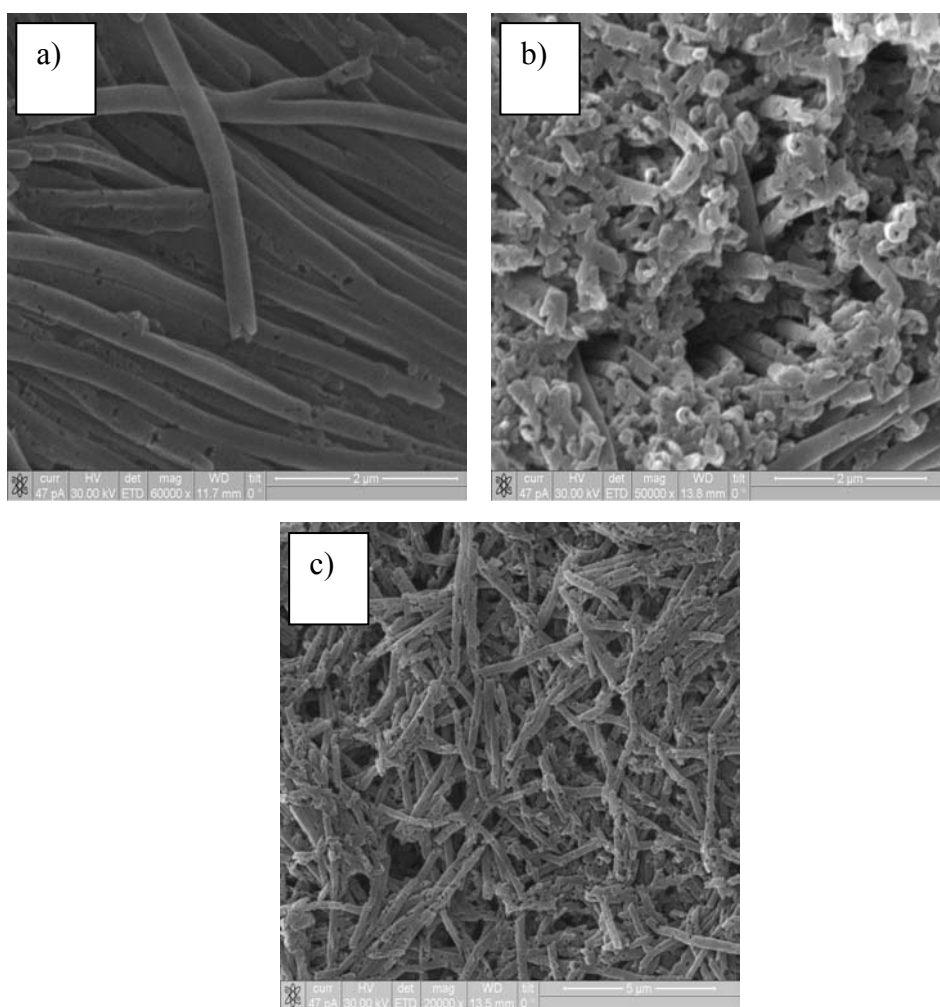


Fig. 4 – SEM images of the polyaniline electropolymerized in the pores of alumina template from solution of  
 a) 0.1M aniline + 0.5M  $\text{H}_2\text{SO}_4$  by potentiostatic method; b) 0.1M aniline + 0.75M  $\text{H}_2\text{SO}_4$  by cyclic voltammetry at high magnification; c) 0.1M aniline + 1M  $\text{H}_2\text{SO}_4$  by potentiostatic method.

The influence of the electrolyte concentration can be seen. As the  $H_2SO_4$  concentration increases, it induces a more open morphology. The integrity of the nanotubes as the  $H_2SO_4$  increases is slightly

poorer due to the hydrolysis, which is confirmed by the broken pieces observed in the images in figure 4c.

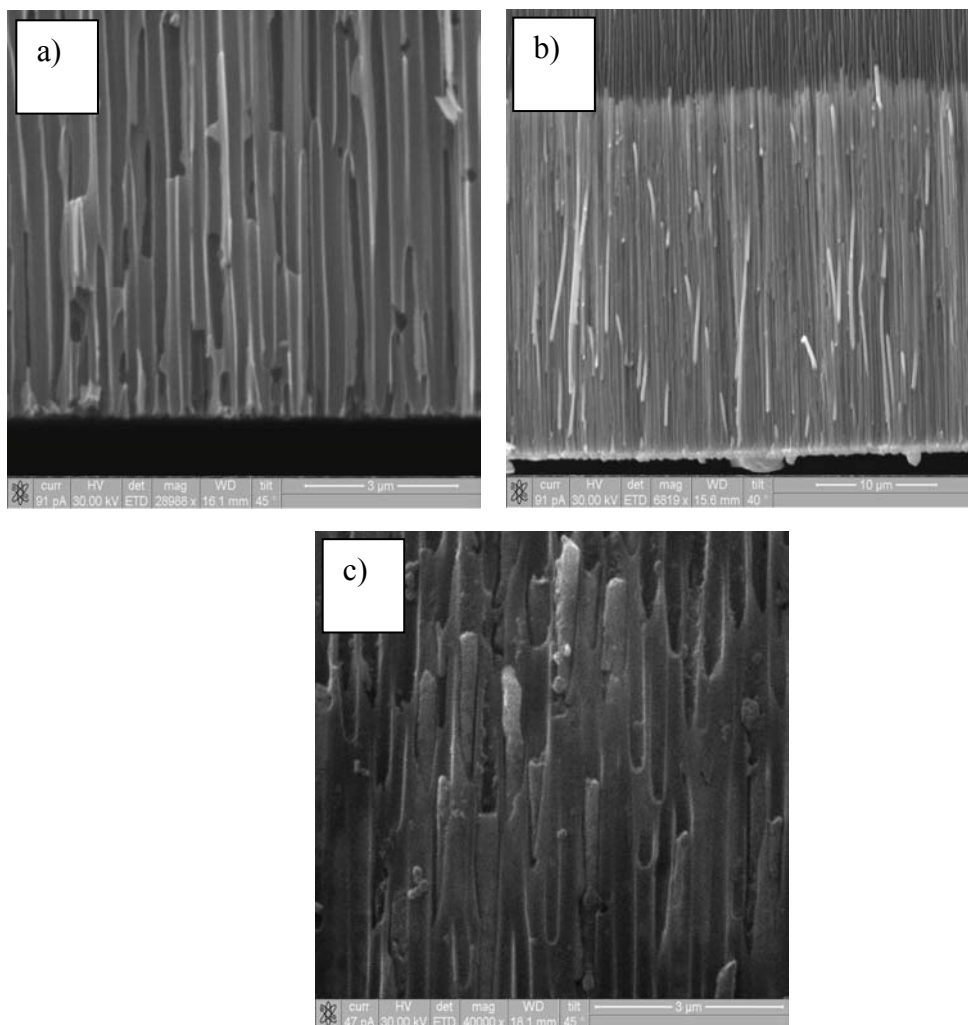


Fig. 5 – SEM images of anodic alumina template a) empty; b) with copper nanowires and c) with copper nanowires embedded in the polyaniline nanotubes.

Further, the template-based deposition of the copper nanowires into the polyaniline nanotubes was studied. For comparison, copper nanowire deposition was performed in the pores of anodic alumina template at a constant potential of -300 mV.

The deposition took place from a solution of  $150 \text{ g L}^{-1} \text{ CuSO}_4 + 25 \text{ g L}^{-1} \text{ H}_2\text{SO}_4 + 5 \text{ g L}^{-1} (\text{NH}_4)_2\text{SO}_4$ . Then, the copper nanowires were grown into the polyaniline nanotubes by so called "second-order-template" method. As the first step, the polyaniline nanotubes were grown potentiostatically at 900 mV. In figure 5 one can see the images of the template before the deposition, filled with copper nanowires and at last, filled with the copper nanowires enveloped in the polyaniline nanotubes. The copper deposition

has a high filling factor as well as the copper deposition into the polyaniline nanotubes.

To assess the deposition of the copper nanowires into the polyaniline nanotubes, energy dispersive X-ray spectroscopy (EDAX) was performed for the polyaniline nanotubes obtained by potentiostatic deposition, before the copper deposition and after it.

The template was removed in NaOH and the samples were Au sputtered before SEM and EDAX analyses. As it can be seen in fig. 6, the obtainment of the polyaniline is clear by the content in the correspondent elements. After the copper deposition, it is observed that the samples contain Cu, fact which confirms the deposition of the copper nanowires into the polyaniline nanotubes.

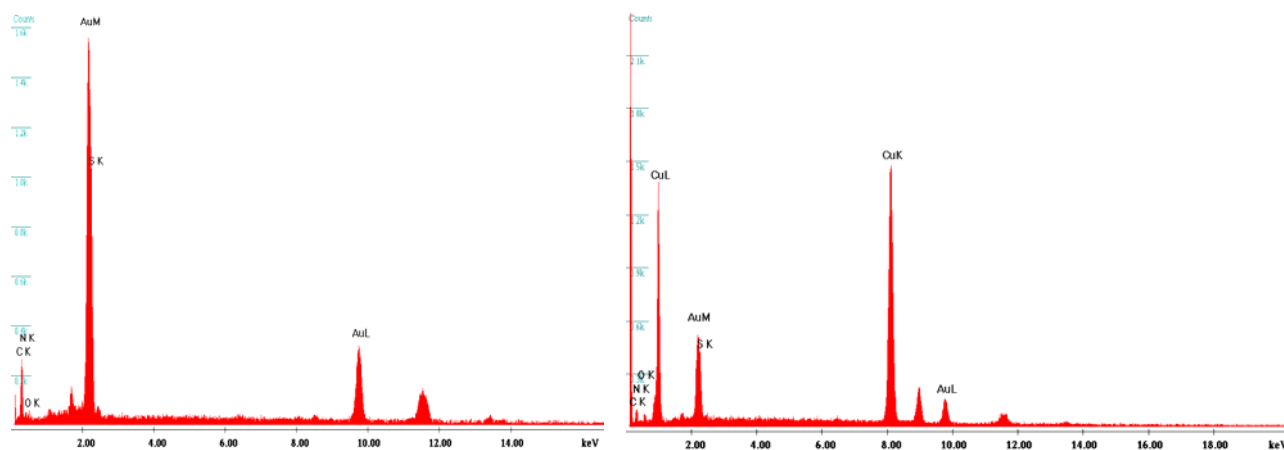


Fig. 6 – EDAX microanalyses of the polyaniline nanotubes a) before and b) after the copper nanowires deposition (after dissolution of the template).

## CONCLUSIONS

The electrochemical synthesis of polyaniline nanotubes in aqueous  $\text{H}_2\text{SO}_4$  solutions was investigated. Highly ordered PANI nanotube arrays were electropolymerized through a template-based method using anodic porous alumina membranes.

Increasing the  $\text{H}_2\text{SO}_4$  concentration during growth induces a transition from more dense to a poorer integrity nanotubes. The nanotube morphology correlates with nucleation and growth mechanisms deduced from current-time transients. At high anodic potential (900 mV), the current transient data fit a 3D diffusion-controlled nucleation and growth model.

An array of copper nanowires enveloped in polyaniline nanotubes was successfully prepared by the "second-order-template" method. As the first step, an array of the polyaniline nanotubes was synthesized in the pores of an alumina membrane, then copper nanowires were fabricated by electrochemical deposition of the copper into the polyaniline nanotubes, as it was confirmed by the results obtained.

The most appealing field for such structures it is at the moment related to sensors (e.g. magnetic field sensors based on GMR effect, photodetectors based on segmented nanowires).

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