Supporting information

Innovative anodic treatment to obtain stable metallic silver micro-patches on TiO_2 nanotubes: Structural, electrochemical, and photochemical properties

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1S. Chronoamperometric measurements

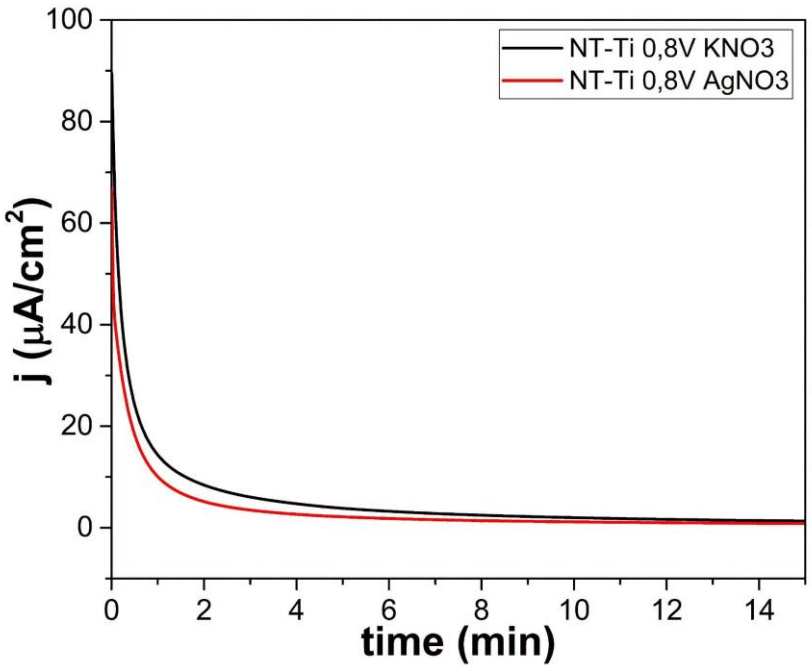

Figure 1S. Current *vs*. time records during the anodization at +0.8V

Figure 1S shows the chronoamperometric record corresponding to +0.8V anodization step to form Ag-NT-Ti micropatches.

The titanium samples with nanotubes were immersed in KNO_3 (NT-Ti) or $AgNO_3$ (Ag-NT-Ti) solution. Subsequently, the anodization at +0.8V was performed in each solution and the transient currents were recorded (Figure 1S).They show the anodic current contribution due to additional TiO_2 formation, slightly lower in case of Ag-NT-Ti.

2S. OCP records of NT-Ti in KCl solution after the +0.8V anodization process

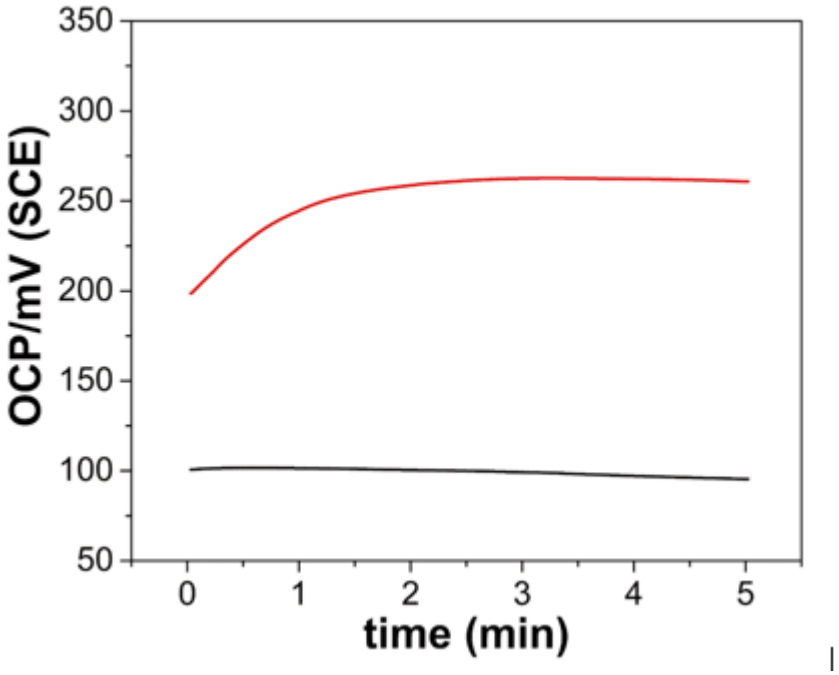

Figure 2S. OCP measurements performed in KCl solution immediately after anodizing at +0.8V (SCE) in $AgNO_3$ (Ag-NT-Ti,red) or in KNO_3 (NT-Ti, black).

After anodizing at +0.8V the circuit is opened, subsequently the NT-Ti and Ag-NT-Ti samples are immersed in KCl solution and the OCP is recorded for 5 min (Figure 2S). Stable potential values are reached after 3 min. Following these measurements the samples were annealed.

3S. Determination of TiO_2 nanotube thickness by indentation.

Figure 3S shows the pyramid-shape cavity formed during indentation using a pyramid diamond tip. The button of the nanotubes can be distinguished and the yellow arrow indicates the greater depth where nanotubes can be found. This depth (h) is considered as the average depth of nanotubes and was calculated using the following equation:

$$h = \frac{d}{2 \times tan\left(\frac{\theta}{2}\right) \times \sqrt{2}}$$

Where h is the indent depth (mm), d is the average length of the diagonal (mm), and **ϴ** is the angle of the indenter (136 degrees) (rad).

The calculated value of h was=9.6 μm.

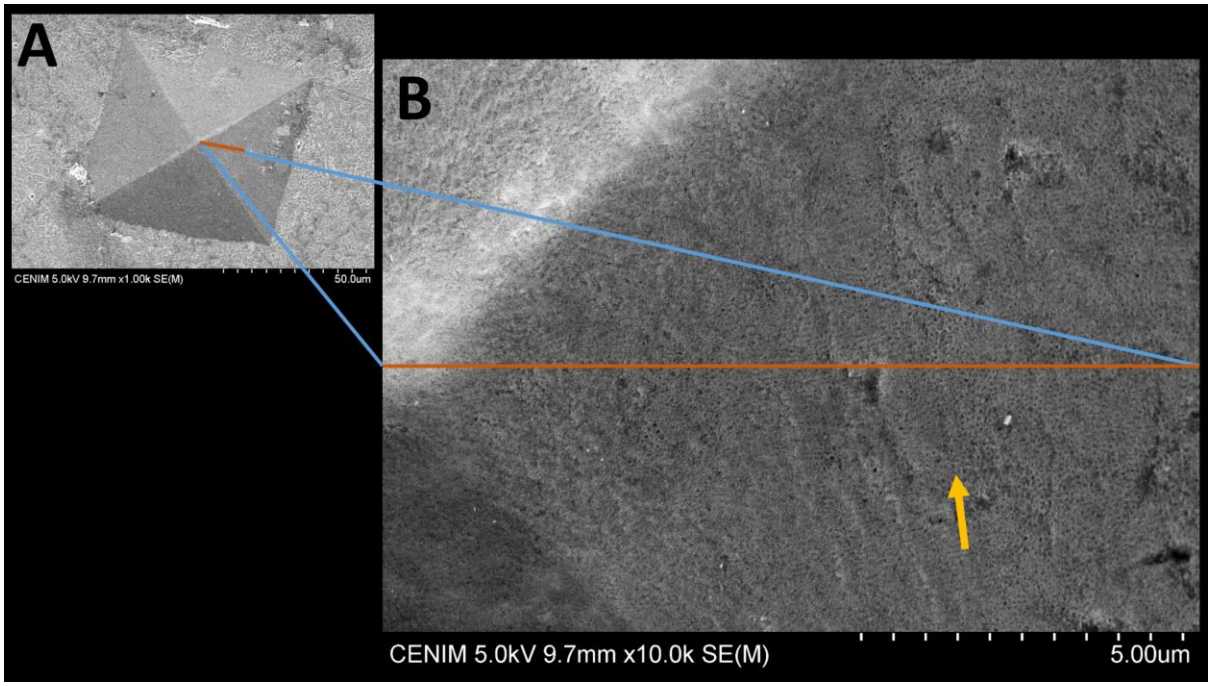

Figure 3S. (A) SEM image of indentation made using a pyramid diamond tip (Vickers) (1kg); (B) SEM image from one of the pyramid-shape cavity where the arrow shows a zone with the homogeneous bottom of the nanotubes.

4S. Determination of Eg values

Figure 4S shows the Tauc plot for NT-Ti and Ag-NT-Ti. The band gap energies obtained from the curves were 3.27 and 3.26 eV for NT-Ti and Ag-NT-Ti respectively.

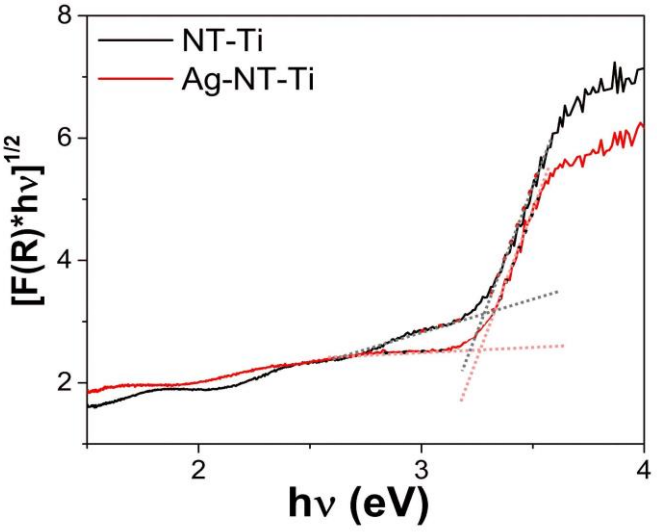

Figure 4S. Tauc plot for NT-Ti (black) and Ag-NT-Ti (red) samples. The graphical determination of E_g is shown with dotted lines.