Synthesis of High Effective Surface Area Silver Nanoparticles Embedded in Porous Alumina Matrix Using the Melt Spinning Process

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Abstract

One of the most relevant uses for the Ag NPs (nanoparticles) is their application on the industry as catalytic material [1, 2]. The catalytic activity of the Ag NPs directly depends on the particle sizes and their distribution [3]. The chemical reduction approach is considered as the most appropriate technique to produce large quantities of nanoparticles with controlled size [4, 5]. Hence, is important to understand that this method uses reactants that can provoke potential risks for the environment and health [5]. The porous anodization of aluminum followed by electrodeposition is a well-known process to obtain metal nanoparticles or nanowires of noble metals as silver [6–8].

In the present work, we developed a new route for the fabrication of Ag nanoparticles embedded in a dielectric matrix (alumina) by the two-step porous anodization of a thermally treated (quenched) alloy using the melt spinner technique. A pro-eutectic Al-Ag alloy (95.25 %wt. Al) was molten and gradually heated to 780 °C using an induction oven and kept at that temperature for 20 minutes before quenching in the melt spinner. Then, a porous anodization process was performed in order to obtain a highly ordered nanotube array. The anodization was performed in 0.3 M oxalic acid solution applying a current density of 50 $mV \cdot cm^{-2}$ for 15 minutes. The structure and morphology of the aluminum oxide with precipitated silver were characterized by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

Fig. 1A shows the SEM image of the surface of the anodized sample evidencing the presence of eutectic Ag in a lamellar structure alongside Ag NPs with a mean diameter of 100 nm on top of the aluminum oxide layer. The cross-section (Fig. 1B) shows that the Al_2O_3 nanotubes formed during the anodization are 9.7 µm long and 200 nm wide, with incrusted Ag NPs on the regular nanotubular layer.

The aluminum oxide layer was physically separate by stripping and characterized by TEM. Fig. 2A shows a typical formed nanotube with a mean diameter of 200 nm. On top of the nanotube Ag NPs are present with a diameter varying from 7 to 18 nm. The TEM/EDS elemental composition analysis that was performed (Fig. 2B), the spectra of the surface (marked as “I’) shows that it is formed of Al-Ag, while the nanoparticles (marked as “II”) contain 99 %at. of silver. The size distribution of the Ag NPs determined by TEM imaging of the surface (Fig. 3A) showed that 95% of the Ag NPs have equivalent diameters smaller than 40 nm, ranging the diameters between 4 and 87 nm, as seen in the histogram of Fig. 3B. Moreover, it is noteworthy that 50% of the nanoparticles have an equivalent diameter between 4 and 10 nm. Consequently, it is confirmed that by a new route evolving porous anodization Ag NPs with sizes ranging between 4 and 87 nm can be produced randomly dispersed on a porous aluminum oxide surface.

References

[1] McFarland AD, Van Duyne, RP, Nano Letters, **3** (2003) 1057-1062.
[2] Köhler JM, Abahmane L, Wagner J, Albert J, Mayer G, Chemical Engineering Science, **63** (2008) 5048-5055.
[3] Zhang J, Chen P, Sun C, Hu X, Applied Catalysis A: General, **266** (2004) 49-54.
[4] Leopold N, Lendl BA, The Journal of Physical Chemistry B, **107** (2003) 5723-5727.
[5] Zhang W, Qiao X, Chen J, Materials Science and Engineering: B, **142** (2007) 1-15.
[6] Huber CA, Huber TE, Sadoqi M, Lubin JA, Manalis S, Prater CB, Science, **263** (1994) 5048-5055.
[7] Yi JB, Pan H, Lin JY, Ding J, Feng YP, Thongmee S, Liu T, Gong H, Wang L, Advanced Materials, **20** (2008) 1170-1174.
[8] Zhang J, Kielbasa JE, Carroll DL, Materials Chemistry and Physics, **122** (2010) 295-300.

Figures

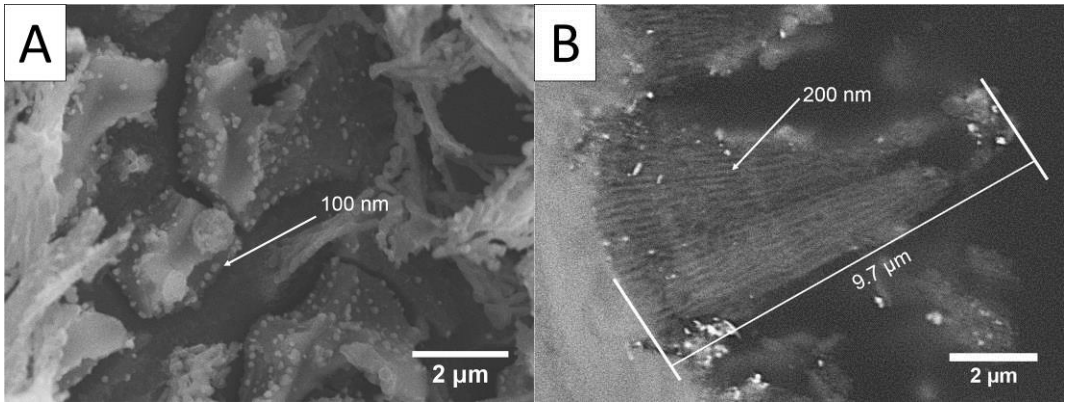

Figure 1. (A) SEM image of the oxide surface containing Ag NPs. (B) Cross-section SEM image of formed Al_2O_3 nanotubes.

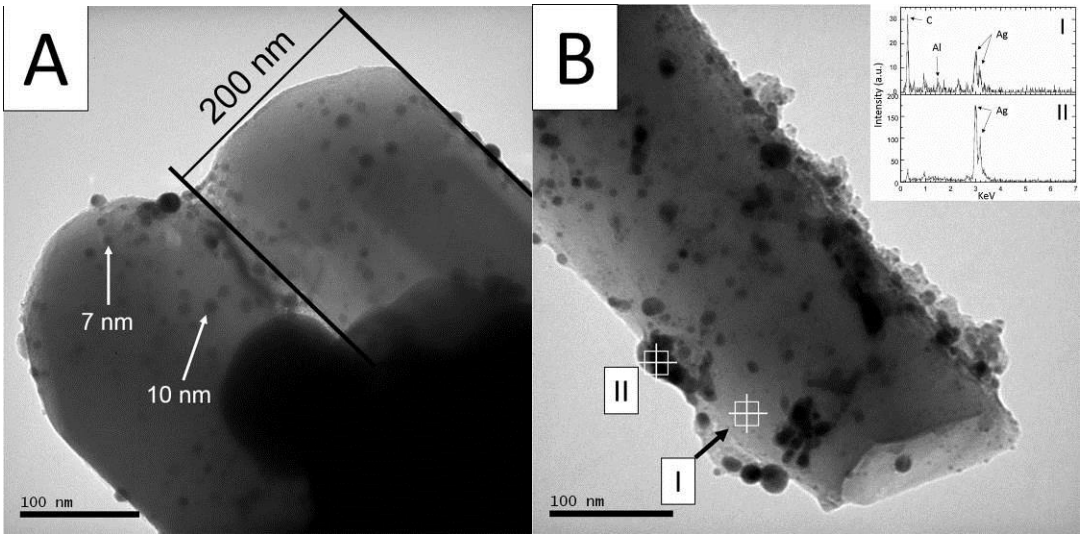

Figure 2. (A) TEM image of formed Al_2O_3 nanotubes with embedded silver nanoparticles. (B) TEM image of nanotube showing the areas of EDS analysis. The insert shows the obtained spectra.

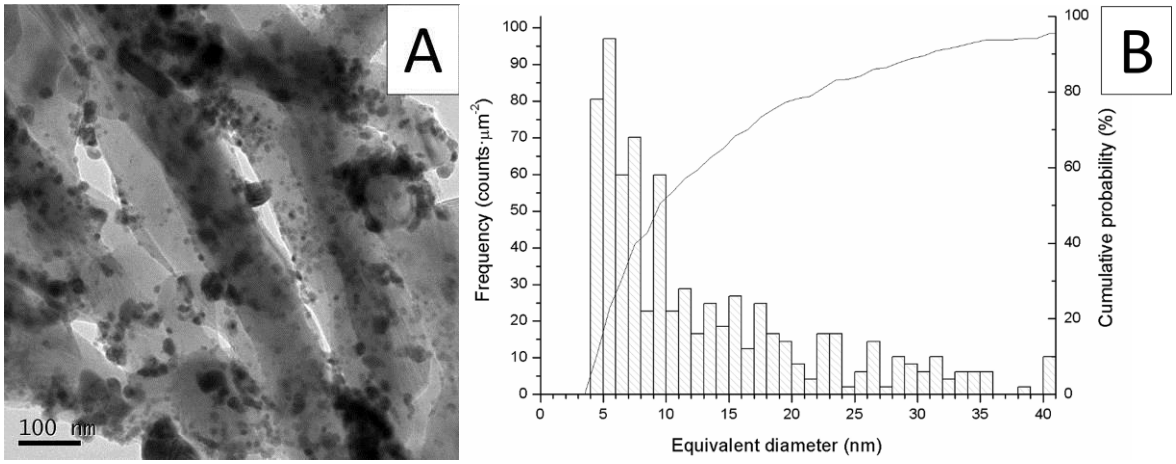

Figure 3. (A) Area selected for the distribution analysis by TEM and (B) histogram of the frequency per area *versus* the equivalent diameter of the silver nanoparticles and the cumulative probability.