

GROWTH AT LOW TEMPERATURES OF AG@TiO₂ NANO-FIBERS BY PLASMA DEPOSITION

A.Borras¹, A. Barranco¹, J.P. Espinós^{1,2}, F. Yubero¹, J. Cotrino^{1,3}, A.R. González-Elipe^{1,2}.

¹*Instituto de Ciencia de Materiales de Sevilla (CSIC-Univ. Sevilla). Avda. Américo Vespucio 49. 41092 Sevilla (Spain) and Departamentos de ²Química Inorgánica and ³Física Atómica Molecular y Nuclear de la Universidad de Sevilla.*

Nanometric-scale rods, fibres or similar nanostructures of oxide materials, in particular TiO₂, are usually prepared by means of chemical or electrochemical routes. These methods usually involve different steps of drying, heating or annealing at high temperature what might hamper their use when mild conditions are a requisite or when the synthesis has to be carried out in a single step. These shortcomings can be circumvented by plasma enhanced chemical vapour deposition (PECVD), a method that works at virtually any temperature and that permits the synthesis of the nanofibres in a single step. Carbon nanotubes (CNT) constitute a clear example of the use of electrical discharges or plasmas for the synthesis of nanostructures at low temperatures in a single step. In the present work, we report about the synthesis of supported Ag@TiO₂ core-shell nanofibres by a new method based on the PECVD of titanium oxide on a silver substrate at $t > 130$ °C.^[1] To our knowledge, this is the first time that plasma deposition has been successfully applied for the synthesis of inorganic supported nanofibers at low temperatures.

Fibres of several microns length and a thickness, varying according to the experimental conditions between 30 and 400 nm were produced by our method. As an example, Fig. 1 shows a series of SEM micrographs for preparations under slightly different conditions. The observed fibres consist of one inner core made of a single crystalline silver thread of ca. 20 nm thickness and an external layer of either amorphous or crystalline anatase. The thickness of this external layer can be varied by just adjusting the TiO₂ deposition time. Based on the morphology and other characterization results of these nano-fibres it has been proposed that the fibres grow according to a new “volcano” type mechanism.

To justify this mechanism, in the present work we have tried to get a deeper insight into the factors that, affecting both the silver substrate and the plasma itself, may be controlling the formation of the supported Ag@TiO₂ nanofibers. With this aim, we have performed a series of experiments by X-ray photoemission spectroscopy (XPS), optical emission spectroscopy (OES) and scanning electron microscopy (SEM). The studied systems have been selected to address and demonstrate specific issues of this “volcano” type mechanism. Thus, SEM analysis has been used to characterize the final morphologies of three different systems, namely TiO₂ layers plasma deposited on complex substrates formed by a silicon wafer with small Ag or Pt particles on its surface, Ag@TiO₂ nano-fibres formed on the complex-shaped silver substrate as a function of deposition time and the surface morphology of a silver foil subjected to plasma oxidation for increasing periods of time. “In-situ” XPS has been used to study the plasma growth of TiO₂ on a silver foil. Meanwhile, OES has provided information about the type of titanium species formed in the plasma during deposition. From the different experimental evidences gained with these experiments some clues are obtained to account for the main factors that may be controlling the formation of the Ag@TiO₂ core-shell nanofibers. Potential applications of these systems as light switchable superhydrophobic coatings or as efficient photocatalysts are presented.

The used methodology can be also used for the preparation of fibres of other oxides and selected examples are shown.

References

1.- A. Borrás, A. Barranco, F. Yubero, A.R. González-Elípe. *Nanotechnology* 17 (2006) 3518

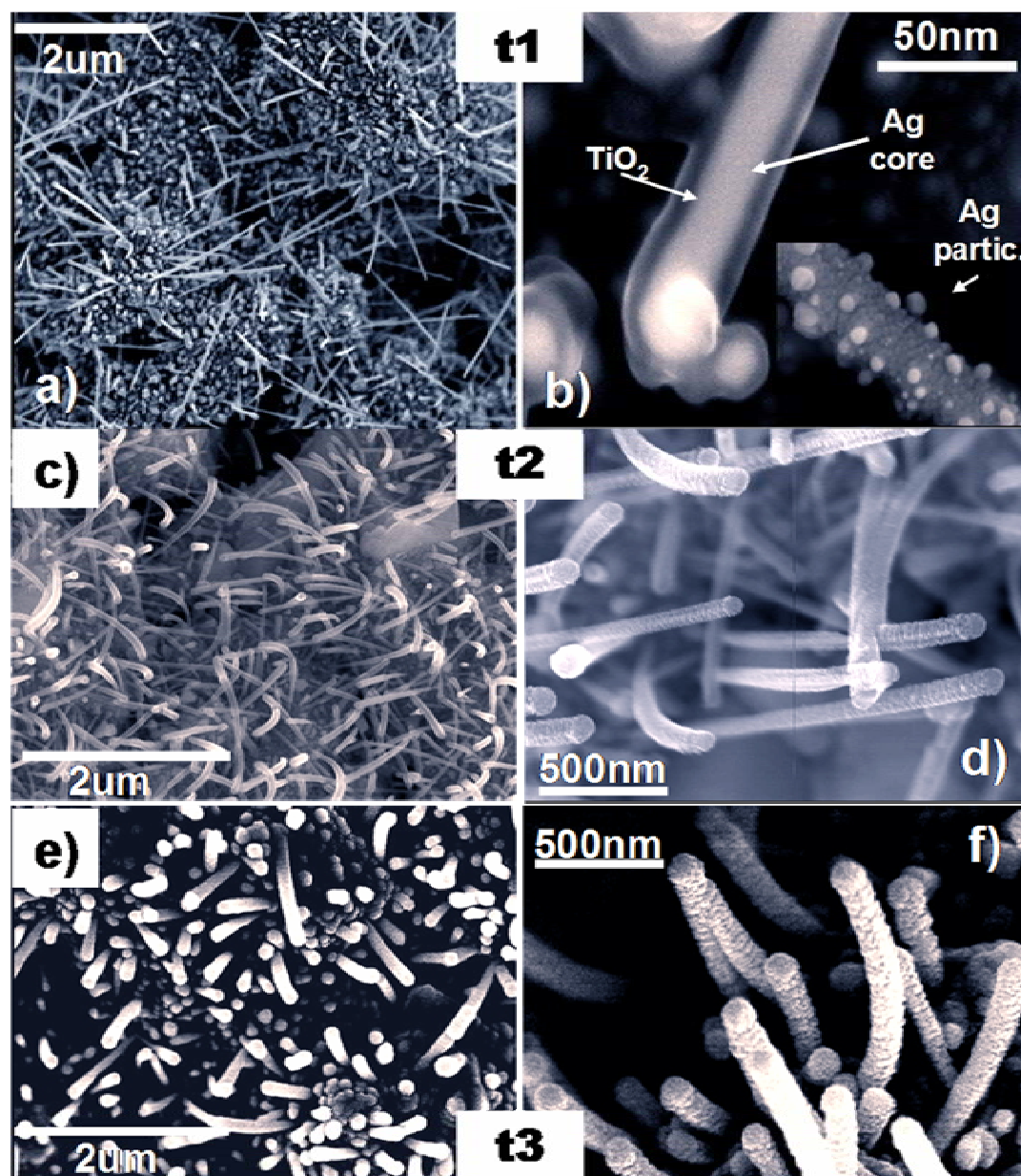


Figure 1.- Normal SEM images for Ag@TiO₂ nanofibres plasma deposited at 130 °C for increasing periods of time from t1 to t3 (see text). Images have different magnification scales to show the high density of fibres formed on the substrate (left images) and their thickness and other morphogological characteristics (right images). The inset in image b) correspond to a fibre with small silver particles on its surface; fibres of this kind are occasionally found at the beginning of the deposition.