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New Insights into the Growth Mechanism of WO_3 Gels by *In-situ* Liquid-Phase TEM and Time-Resolved DLS

Charles Sidhoum[1*], Mateusz Odziomek[2], Dris Ihiawakrim[1], Doru Constantin[3], François Schossler[3], Clément Sanchez[2,4], and Ovidiu Ersen[1]

[1] Institut de Physique et Chimie des Matériaux de Strasbourg, Strasbourg, France.
[2] Laboratoire de Chimie de Matière Condensé de Paris, Sorbonne Université, Paris, France.
[3] Institut Charles Sadron, Strasbourg cedex, France.
[4] USIAS, University of Strasbourg Institut of Advanced Study, France.

The electrochromic and photocatalytic properties of tungsten oxide (WO_3) find broad applications in display devices, smart windows or degradation of pollutants [1]. The synthesis of WO_3 does not require high temperatures, and soft methods fitting into "chimie douce" concept are well-established [2]. Following the sol-gel routes, it is possible to obtain WO_3 gels by acidification of tungsten salt solutions. The acidification leads to hydrolysis and consecutive condensation first to polyoxotungstate species and further to gel-like structure. Although the process has been studied by various techniques [3], we still lack the understanding on how the charged polyoxometallate species react with each other and form a gel.

Several models have been proposed, based on the condensation of a hypothetical "zero-charge complex" by hydroxylation and oxolation [4]. The recent developments in TEM, in particular the emergence of the in-situ Liquid Phase TEM (LP-TEM), may provide new insight into the nucleation and growth processes of WO_3-based nanostructures, with a particular focus on the early steps of gel formation.

Herein, using the ability of LP-TEM to monitor nanometric processes in real space, we report a first picture of the growth of WO_3 gels. This in situ analysis highlights several possible pathways for the growth mechanism, including the diffusion-limited cluster aggregation process. Indeed, a closer look into the reaction environment (Figure 1) reveals the presence of well-defined clusters, with a nanometric size, which apparently plays the role of elemental bricks for gel formation [5].

To further improve the comprehension of the first growth events, we have also carried out time-resolved DLS measurements for different tungsten salt concentration. As expected, a decrease in concentration (Figure 2b) leads to a decrease in intensity but, at the same time, we find similar sizes (Figure 2a), indicating the presence of precursors of few nm. In complement to DLS data obtained during the first 30 minutes, cryo-TEM studies are ongoing in order to complete the mechanistic picture and to provide a complete description of the growth process.

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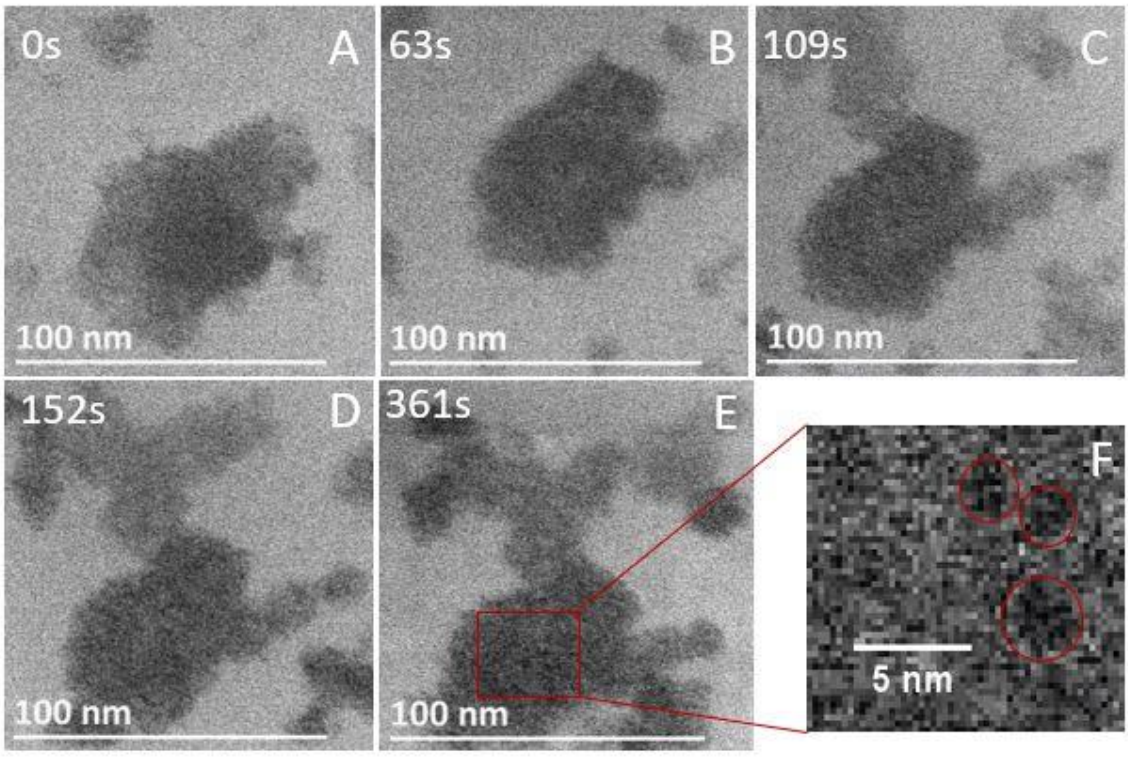

Figure 1. A-E: LP-TEM images of WO_3 gel growing by Diffusion-Limited Cluster Aggregation (DLCA). F: Zoom on the gel structure highlighting the presence of clusters with a few nm sizes.

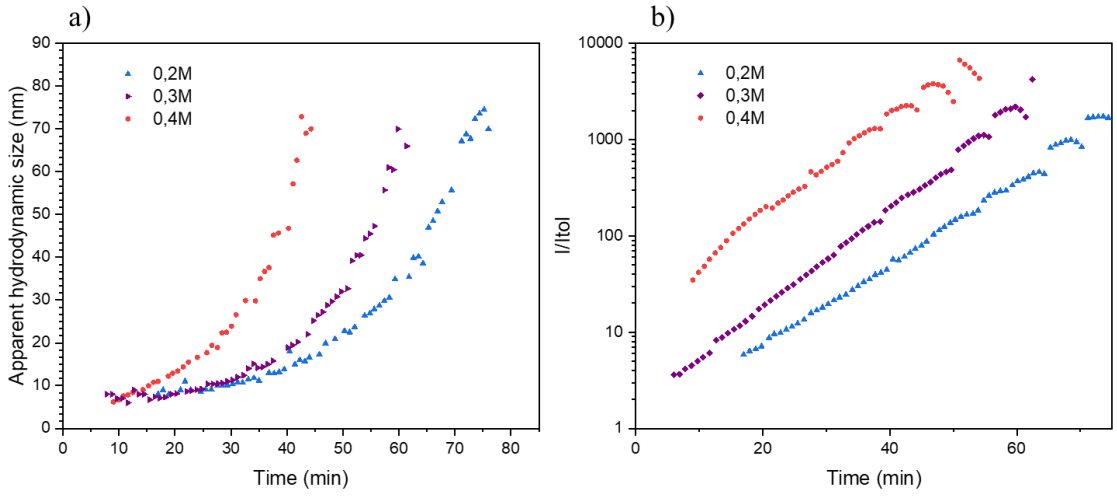

Figure 2. Time-resolved DLS measurements revealing the time evolutions of apparent hydrodynamic size (a) and of the absolute intensity (b) of tungsten gel precursors for different tungsten salt concentrations.

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