Conformal coating of nanoporous γ-alumina using Atomic layer deposition: Spinel formation and luminescence induced by rare-earth doping

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There is presently a real challenge to build nanostructured materials on a large variety of supports and atomic layer deposition (ALD) stands out as the most promising method for coating nanomaterials and more specifically nanoporous materials[1]. There is now increasing interest in nanoporous complex oxides, e.g. ZnO-based spinel type compounds[2]. We have developed a new route towards synthesis of nanoporous spinel using nanoporous γ-alumina particles (γ-ANPs) as a support and by deposition of thin oxide coatings using ALD. For this purpose, a small glass reaction chamber (powder cell) was adapted to a F-120 Sat reactor (ASM) flow type ALD reactor to coat nanoporous micrometer-sized γ-alumina particles (20 – 100μm of diameter) (Fig.1a). These kinds of γ-ANPs are usually used as industrial catalysts supports and more specifically for Fischer-Tropsch process.
In this study, the deposition of ZnO thin films using using $ZnEt_2$ and water as precursors at temperature ranging from 170 to 200ºC will be described[4]. The challenge lies in the capability to completely coat the inside of the particles and the conformity and uniformity characteristics of ALD are essential to the formation of such a smooth coating. In fact, it is possible to fully coat the external surface of γ-ANPs. However, the common flow type system does not allow complete coating of the interior of the particles due to a nanoporosity of about 16nm. A powder cell is then necessary and a careful control of the gas flow enable to improve the internal coating of these nanoporous particles.
The formation of spinel structure was achieved by first depositing a homogeneous and conformal oxide thin film on the surface of the γ-ANPs, which were then annealed under air in order to induce diffusion of zinc inside the γ-alumina structure in order to maintain an open porous structure exploiting the Kirkendall effect[3].This allowed a spinel structure formation without deteriorating the porosity of the nanoporous structure. XRD data measured as a function of annealing temperature showed that $ZnAl_2O_4$ spinel structure formation occurs above 800ºC. EFTEM demonstrates conformal and homogeneous coating of ZnO without any sealing of the pores during the deposition process[5] (Fig. 2). BET measurements also proved a low reduction in specific surface area subsequent to such annealing.
In order to produce highly luminescent robust and inert nanoporous structures that can be used as red-emitting phosphors, the particles were coated with rare earth oxides by ALD using $Dy(thd)_3$, $Er(thd)_3$ or $Eu(thd)_3$ and ozone as precursors at 200ºC. Due to ozone degradation into the pores of the structure, a method of deposition that does not use the powder cell system where only the surface of the particles was coated was employed. However, a high luminescence was observed (Fig. 3) and it is possible to differentiate the coated γ-alumina from the uncoated under UV exposure. Thus a novel synthesis rout for highly porous luminescent spinel particles that can have several potential applications, e.g. as promising tracer, can be used as a component in optoelectronics or as catalyst support will be discussed and.

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Figures

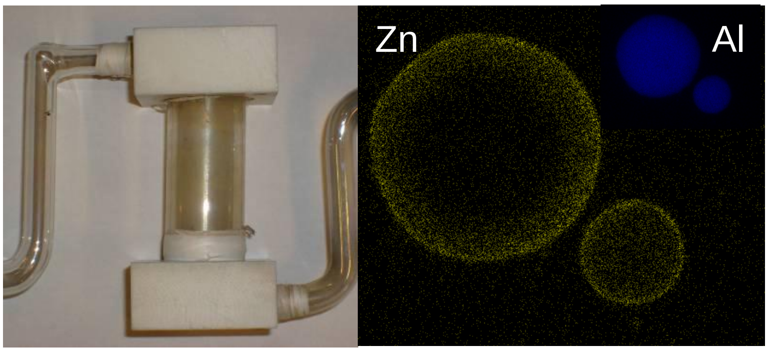

Figure 1: (a) Powder cell adapted to a F-120 Sat (ASM) ALD reactor (b)SEM mapping of cross section of coated γ-alumina (Zn element); inset: mapping of Al element.

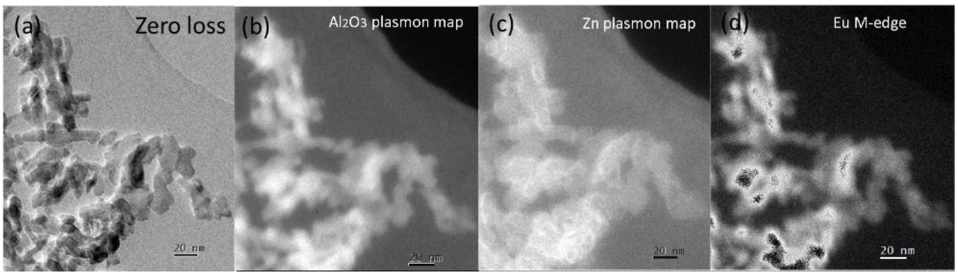

Figure 2: EFTEM pictures of γ-alumina particle coated with zinc oxide and europium oxide: conformal coating of the nanoporous structure.

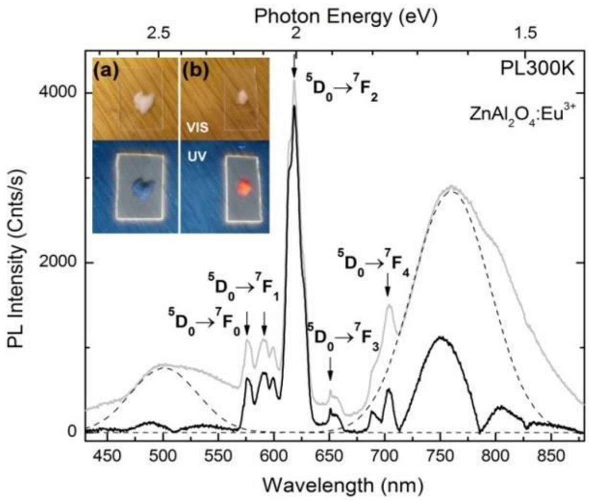

Figure 3: PL spectra upon UV exposure recorded at 300K for γ-alumina particles coated with ZnO and EuO and then annealed at 800ºC.