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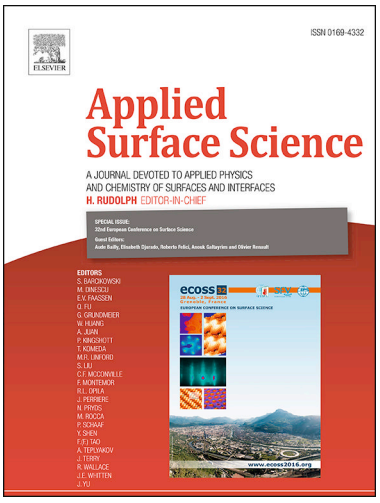

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Two-step growth mechanism of supported Co_3O_4-based sea-urchin like hierarchical nanostructures

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Abstract

Supported 3D hierarchical nanostructures of transition metal oxides exhibit enhanced photocatalytic performances and long-term stability under working conditions. The growth mechanisms crucially determine their intimate structure, that is a key element to optimize their properties. We report on the formation mechanism of supported Co_3O_4 hierarchical sea urchin-like nanostructured catalyst, starting from Co-O-B layers deposited by Pulsed Laser Deposition (PLD). The particles deposited on the layer surface, that constitute the seeds for the urchin formation, have been investigated after separation from the underneath deposited layer, by X-ray diffraction, X-ray absorption spectroscopy and scanning electron microscopy. The comparison with PLD deposited layers without O and/or B indicates a crucial role of B for the urchin formation that (i) limits Co oxidation during the deposition process and (ii) induces a chemical reduction of Co, especially in the particle core, in the first step of air annealing (2 h, 500 °C). After 2 h heating Co oxidation proceeds and Co atoms outdiffuse from the Co fcc particle core likely through fast diffusion channel present in the shell and form Co_3O_4 nano-needles. The growth of nano-needles from the layer beneath the particles is prevented by a faster Co oxidation and a minimum fraction of metallic Co. This investigation shows how diffusion mechanisms and chemical effects can be effectively coupled to obtain hierarchical structures of transition metal oxides.

1. Introduction

Composites based on hierarchical nanostructures of transition metal oxides are very promising materials for various photocatalytic applications, including degradation of pollutants, H_2 production and CO_2 reduction [1, 2]. Their peculiar structure boosts light scattering and harvesting, largely increases the surface

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