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# Effect of La Additive on the Morphology and Photocatalytic Perfomance of 2D $TiO_2$ Nanosheets: Degradation of 4 Chlorophenol

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Over the past years, various aspects of photocatalysis have been reviewed and its importance of for the remediation of air and water pollutants is well documented [1]. $TiO_2$ has been proven to be one of the most widely used photocatalysts for decomposing organic compounds. Some of the strategies employed to increase the solar photoactivity of $TiO_2$ include the addition of a co-catalyst (Pt, $RuO_2$) as well as the doping of $TiO_2$ with non-metal and metal ions [2]. These strategies have led to the discovery of lanthanum-doped $TiO_2$ which is currently one of the most active photocatalysts for the degradation of environmental pollutants. In general, the $La_2O_3$ is usually used as an additive to improve the resistance of some materials against sintering, oxidation and chemical corrosion.

Herein, we use freeze-drying process for the synthesis of ultrafine precursors containing a mixture of aqueous colloid peroxo-polytitanic $Ti^{(IV)}$ acid (PPTA) and $La(NO_3)_3$. The treatment of lyophilized La-PPTA precursor at temperature range 500-950 °C led to the evolution of La modified anatase $TiO_2$ with well-defined 2D nanosheet morphology. The photocatalytic performance of annealed La modified $TiO_2$ materials was evaluated in terms of degradation of 4-chlorophenol (4-CP). The surface and bulk properties of La modified 2D $TiO_2$ nanosheets were investigated *via* surface (XPS, HRTEM) and bulk (XRD, Raman, UV−Vis) experiments.

SEM of the La modified $TiO_2$ materials are in line with our previously published results [3]. The morphology of the precursor is presented in Fig. 1a-b. It was determined that the as obtained material is mainly in amorphous state, which is changed after heat treatment (Fig. 1c-d) and joined crystalline lamellae, identifiable by shape and size, can be observed at temperatures up to 800 °C (Fig. 1e). Such lamellar morphology is a result of the controlled nucleation during the freeze-drying process, which can affect the phase morphology and stability. The crystallization takes place only in 2D direction and the lamellar structure (2D nanosheets) with different degrees of crystallinity is preserved. At 950 °C the 2D nanosheet morphology partly collapsed since anatase-rutile transformation took place (Fig. 1f). The La dopant is working as a structural promoter, which stabilized smaller $TiO_2$ nanocrystals and increased the BET. La additives could be regarded as potential electronic promoters that can widen the band gap of La modified 2D $TiO_2$ photocatalysts. Enlargement of the band gap of Ti_La_650 (Fig. 2a) and Ti_La_800 (Fig. 2b) photocatalysts is attributed to the modification of the 2D $TiO_2$ nanosheet band structure due to spatial confinement of the charge carriers. The photocatalytic degradation of 4-CP and this is affected by altering the structure of the catalysts were also confirmed (Fig. 2c).

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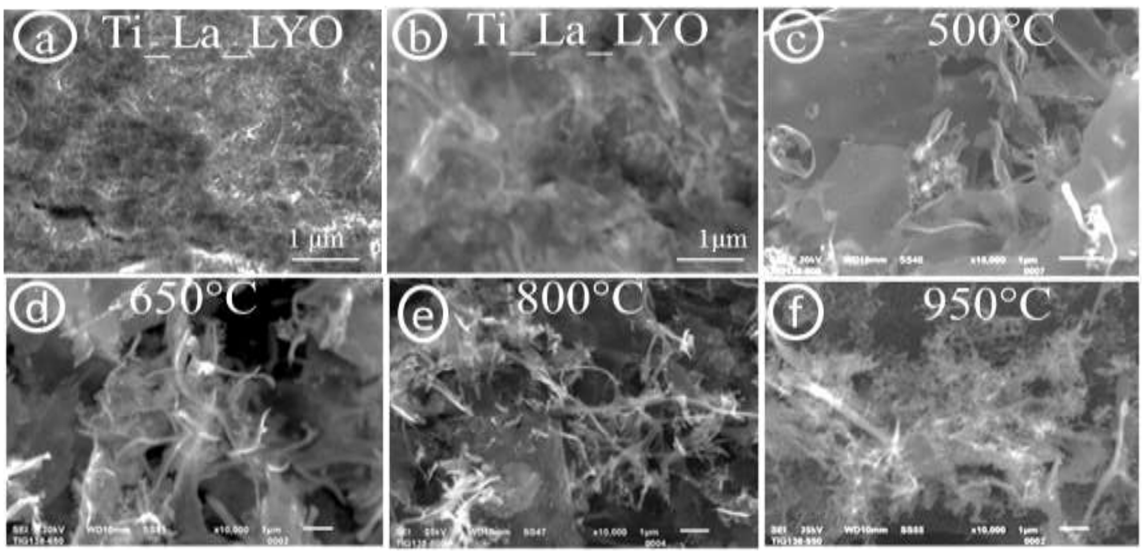


**Figure 1.** SEM micrographs of (a-b) Ti_La_LYO precursor and its post annealed products, (c) Ti_La_500, (d) Ti_La_650, (e) Ti_La_800, and (f) Ti_La_950.

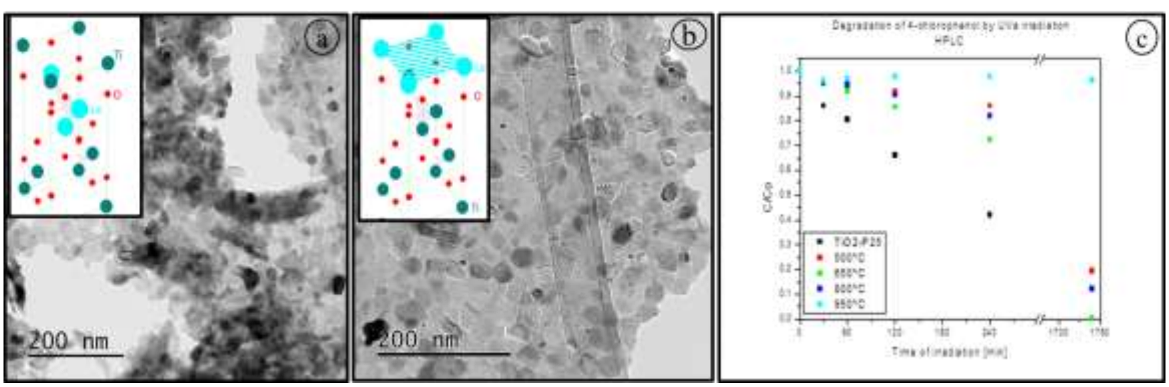


**Figure 2.** HRTEM micrographs of (a) Ti_La_650, (b) Ti_La_800 and its schematic representation by CrystalMaker as inset (c) photocatalytic degradation of 4-CP in the presence of Ti_La_500, Ti_La_650, Ti_La_800, Ti_La_950 and $TiO_2$-P25 catalysts.

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