

## Reduction of TiO<sub>2</sub> by a low-temperature degradation of adsorbed organic solvents

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We discuss how employing a refluxing solvothermal treatment of TiO<sub>2</sub> in organic solvents at mild temperature (120 °C) allows producing blue-colored and reduced titanium dioxide (TiO<sub>2-x</sub>). The treatment, tested for different organic solvents, increases the density of Ti(III) species and the appearance of two optical absorption features: a broad absorption band responsible for the blue coloration and a subgap absorption tail close to the band gap energy.

Experimental analyses based on X-ray photoemission spectroscopy and excitation-resolved photoluminescence suggests that the solvothermal process at 120°C leads to formation of surface and subsurface oxygen vacancies (V<sub>O</sub>). Different solvents have been tested, where ethanol is found to be the most effective. Improved photocatalytic degradation by the processed TiO<sub>2</sub> under VIS illumination is demonstrated, and the possible mechanism involved in the formation of surface V<sub>O</sub> is discussed. The method outlines a very simple, low-cost, and fast procedure to target the formation of V<sub>O</sub> in the TiO<sub>2</sub> surface region.



**Figure 1:** Image P25 powder before (left column) and immediately after (center and right columns) a 24 hours refluxing treatment in three different alcohols (Top row: ethanol; center row: methanol; bottom row: 2-propanol) and at two different oil bath temperatures: T<sub>1</sub>=T<sub>b</sub>+10°C (center column) and T<sub>2</sub>= 120°C. Here T<sub>b</sub> indicates the boiling temperature of the different alcohols.