From highly reactive amorphous tantalum oxide to tantalum nitride. Impact of the nitridation temperature on the optical and photocatalytic properties

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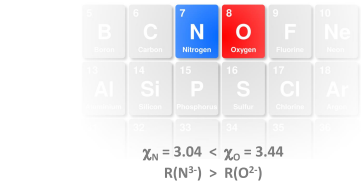
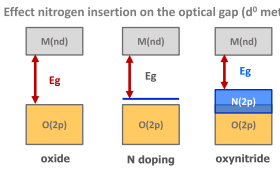
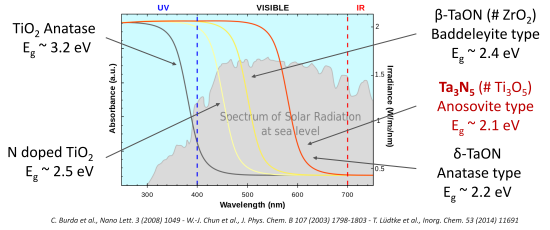
UMR CNRS 6226 Institut des Sciences Chimiques de Rennes (ISCR), Université de Rennes 1, F-35042 Rennes, France

Recently, much further attention has been paid to functional (oxy)nitrides as emerging materials for environmental and energy applications with a focus on the specific tuning properties offered by the nitrogen/oxygen substitution. Among them, **red tantalum nitride Ta_3N_5** is particularly regarded as a visible-light driven photocatalyst because its **narrow bandgap of 2.1 eV** allows for the harvesting of most of the visible range of the solar spectrum. In order to enhance the photocatalytic activity of the material, the morphology of the powder is an important parameter. Thus soft chemistry routes are usually required for the synthesis of the oxide precursor, i.e. Ta_2O_5, as conventional commercial products are usually not suitable due to their micrometric grain size. A better control of the particle size and specific surface area of the oxide precursor also allows for the lowering of the nitridation reaction time and temperature, and for limiting the generation of reduced defects detrimental to optical and photocatalytic properties of Ta_3N_5. However, there is only a few options for the starting materials for the synthesis of the Ta_2O_5 using soft chemistry routes, such as oxalate ($Ta(C_2O_4)_x$), chloride ($TaCl_5$) or alkoxydes ($Ta(OEt)_5$) which are costly and in some cases highly moisture sensitive. We propose here a **simple approach for the amorphization of commercial cristalline Ta_2O_5**, involving the use of potassium bisulfate ($KHSO_4$), in order to improve its reactivity towards ammonia and thus lower the nitridation temperature.

d^0-metal based (oxy)nitrides as visible light absorbers





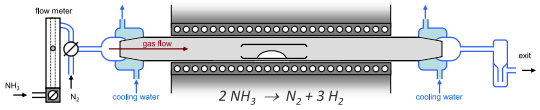


C. Burda et al., Nano Lett. 3 (2008) 1049 - W.-J. Chun et al., J. Phys. Chem. B 107 (2003) 1798-1803 - T. Lüdtke et al., Inorg. Chem. 53 (2014) 11691

Ta_3N_5 from nitridation of cristalline tantalum oxide

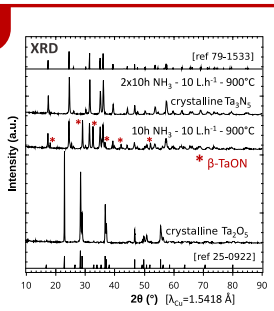
$$MO_x + y\,NH_3 \rightarrow MO_zN_y + {}^3/_2y\,H_2O \qquad z = x - {}^3/_2y$$

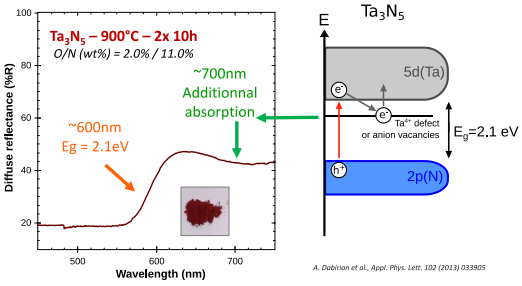
600 °C ≤ T ≤ 1000 °C



!!! Reductive atmosphere → formation of reduced type defect !!!

!!! Charge balance 3 O^{2-} = 2 N^{3-} + Vac → anion vacancies !!!





A. Dabirian et al., Appl. Phys. Lett. 102 (2013) 033905

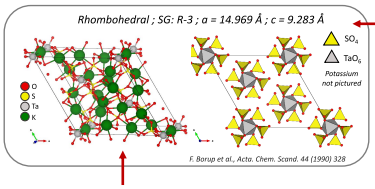
Tantalum precursor from hydrolysis of $K_7Ta(SO_4)_6$

Commercial crystalline Ta_2O_5
+
Large excess of $KHSO_4$

600°C – 2h under air

$K_7Ta(SO_4)_6$ + $K_2S_2O_7$

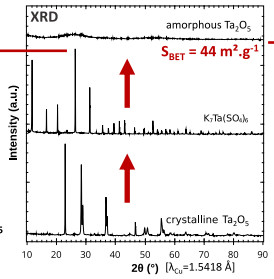
washed with water



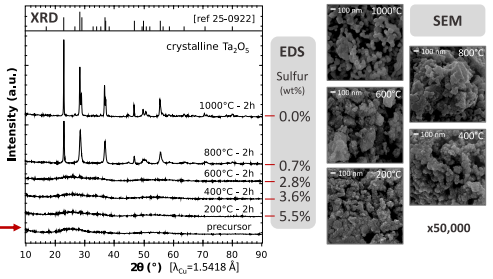
Crystalline $K_7Ta(SO_4)_6$

Hydrolysis with 0.1M HCl

Amorphous Ta_2O_5

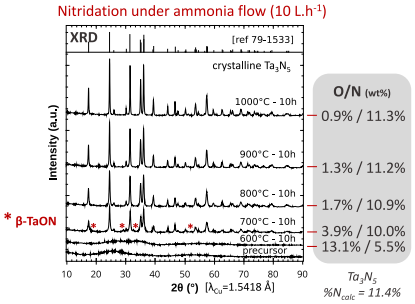


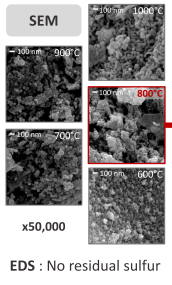
Calcination under air



Effect of nitridation temperature on the optical absorption and the photodegradation of Methylene Blue

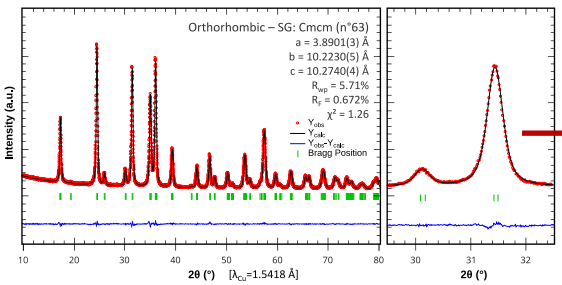
Nitridation under ammonia flow (10 $L.h^{-1}$)





EDS : No residual sulfur

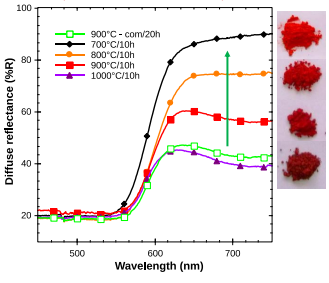
Rietveld refinement – Nitridation at 800°C for 10h



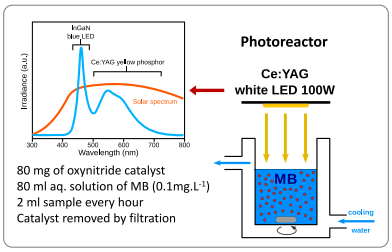
Cristallite size = 25 nm

S_{BET} = 34 $m^2.g^{-1}$

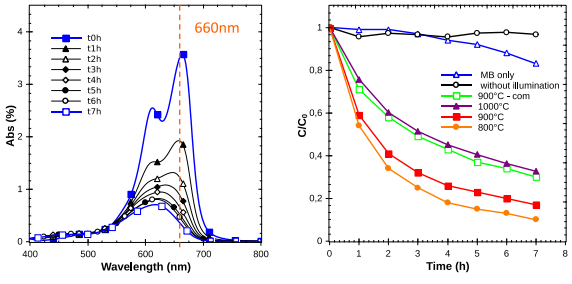
Absorption vs. Nitridation temperature



Photocatalytic tests conditions



Methylene Blue photodegradation monitored by UV/Vis at 660 nm



corresponding author : francois.chevire@univ-rennes1.fr