

Photocatalytical Studies on Multiply Doped Visible Light Active $Zn_xTi_yO_{w-x}N_x$ layers

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25 years of research devoted to semiconductor photo-catalysis brought about several new materials concepts currently explored in environmental sciences, solar cell technologies and preparative “green” chemistry. A real breakthrough is however yet to come because photo-stable non-toxic visible-light harvesting nano-architectures are still not available.

At least two strategies of “doping” exist that shifts the optical spectra of white pigments TiO_2 and ZnO from the UV into the visible spectral range. The first route is based on embedding transition metal cations (Fe^{3+} , Pt^{4+} , V^{5+} etc.) or their complexes into the nanocrystals. Of particular interest to us is the second recently reported sputtering of metal oxide targets in $Ar-N_2$ gas mixtures offering colored powders and layers of zinc^[1]- and titanium^[2] oxynitrides.

In our work, we developed two new wet chemical routes to colored $Zn_xTi_yO_{w-z}N_z$ powders and nanocrystalline waveguides on glass. The first route starts with the synthesis of alcoholic ZnO nanocolloids using $[Zn_4O(Ac)_6]$ precursor. The condensed nanocolloids containing 5 nm large Wurtzite nanocrystals are then reacted with titanium tetraisopropoxide ($Zn/Ti = 1$) to give yellow colored amorphous sols. A more straight forward second route employs a refluxing of zinc acetate in titanium butoxide solvent until similarly colored sols are formed. The resulting alcoholic cluster solutions are remarkably photosensitive. In the presence of sun light, they turn slowly their color from initially yellow to deep-blue (see Figure 1). This coloration can be reversed by introducing oxygen into the cluster sol that suggests a possible presence of long-lived trapped electrons within the existing “Zn-O-Ti” nanostructures.

The wet films prepared from these precursor sols are pre-sintered at $400^\circ C$ in air to remove organic residues and subsequently annealing under ammonia gas at temperatures between $550^\circ C$ and $800^\circ C$ to shift the optical absorption edge into the visible (see Figure 2). In this process, a replacement of oxygen by nitrogen takes place that has been proved in XPS- and complementary EELS-studies^[3]. An XRD investigation of the nanopowders and thin films revealed the presence of *Inverse Spinel* nanostructures with sizes around 10 nm.

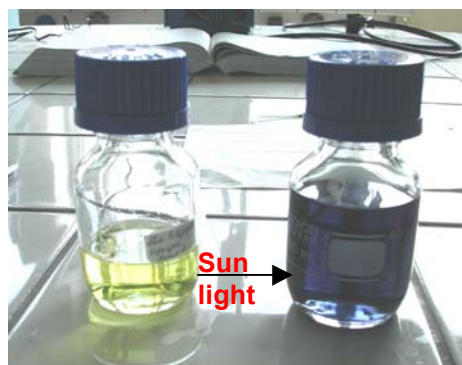


Fig. 1 Photosensitive alcoholic Zn-O-Ti-cluster solutions employed in the processing of vis-light active photocatalytic coatings.

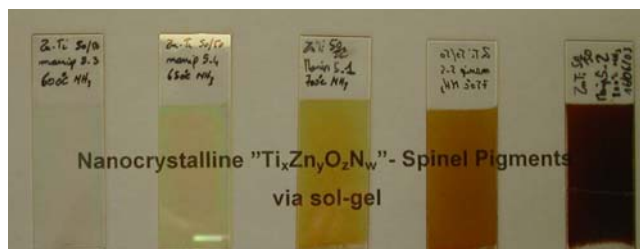


Fig. 2 Coloration of $Zn_xTi_yO_w$ thin films observed after the nitridation under ammonia gas at different temperatures ($400^\circ C$ till $800^\circ C$, from left to right).

In our photocatalysis studies, a degradation of Methylene Blue (MB) was tested as a model reaction to evaluate the visible light activity of yellow colored $Zn_xTi_yO_{w-z}N_z$ thin films prepared by the second route. Figure 3 below (at left hand side) compares the optical absorption spectra of the nitridated and non-nitridated films used in this study. A strong shift of the steep absorption edge initially located at 350 nm to around 450 nm can be seen as the result of the film nitridation process at 600°C. The figure at right hand side shows optical spectral changes detected before and during the exposure of MB-infiltrated nitridated film sample to the visible part of a Xenon lamp (> 420 nm):

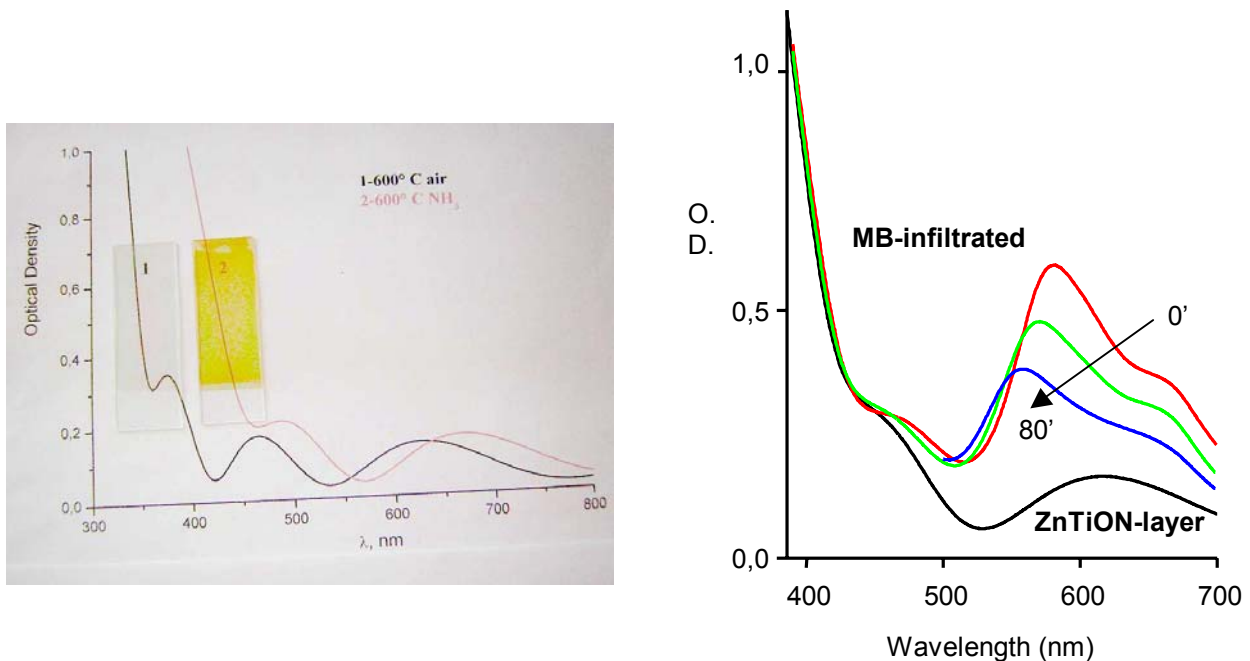


Fig. 3 At left: UV-vis optical spectra of 500 nm thick $Zn_xTi_yO_{w-z}N_z$ film before and after the nitridation process (15 minutes under ammonia atmosphere at 600°C). The presence of interference fringes beyond the absorption band edge reflects a low surface roughness, thus a high optical quality of the photoactive waveguides; at right: UV-vis absorption spectra of MB-infiltrated $Zn_xTi_yO_{w-z}N_z$ film before and during the visible light activated Methylene Blue photo-degradation.

From these preliminary studies, following major results are of note. Firstly, MB-infiltration into the above porous waveguides significantly shifts the maximum of the MB-absorption towards shorter wavelengths. The absorption peak of the MB monomers dispersed in aqueous solution, typically observed at 660 nm is significantly shifted to 570 nm after the infiltration into the porous films. This so-called metachromasy has not been observed up to now on bare titania powders or films. It seems that the presence of interfacial zinc might be responsible for the specific interaction of the MB with the photocatalyst interfaces causing a stronger electron localization within the MB molecules. Secondly, prolonged irradiation of MB-infiltrated coatings in oxygen containing aqueous solution progressively degrades and blue-shifts the optical absorption spectrum of the MB molecules. In a complementary FTIR-study we observed a concomitant disappearance of the characteristic MB vibrations that proves that photodegradation process of this textile dye took place under visible light irradiation conditions.

References

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