Peculiarities of iron titanate thin films synthesis and their physicochemical properties

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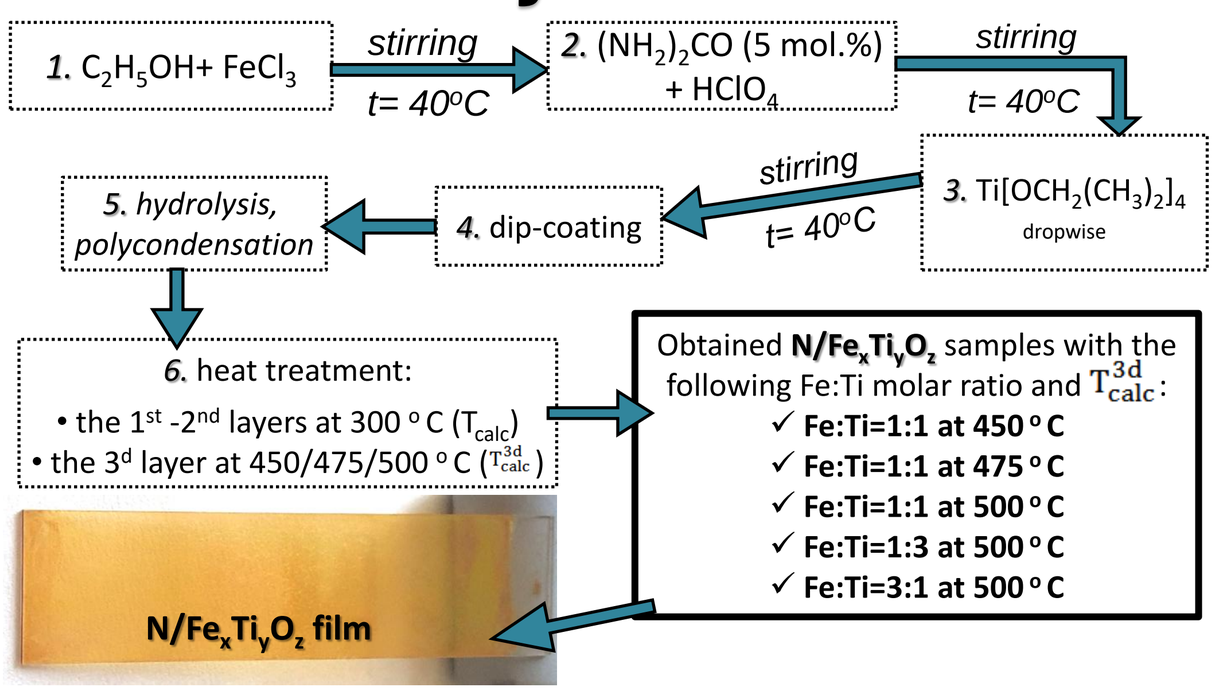
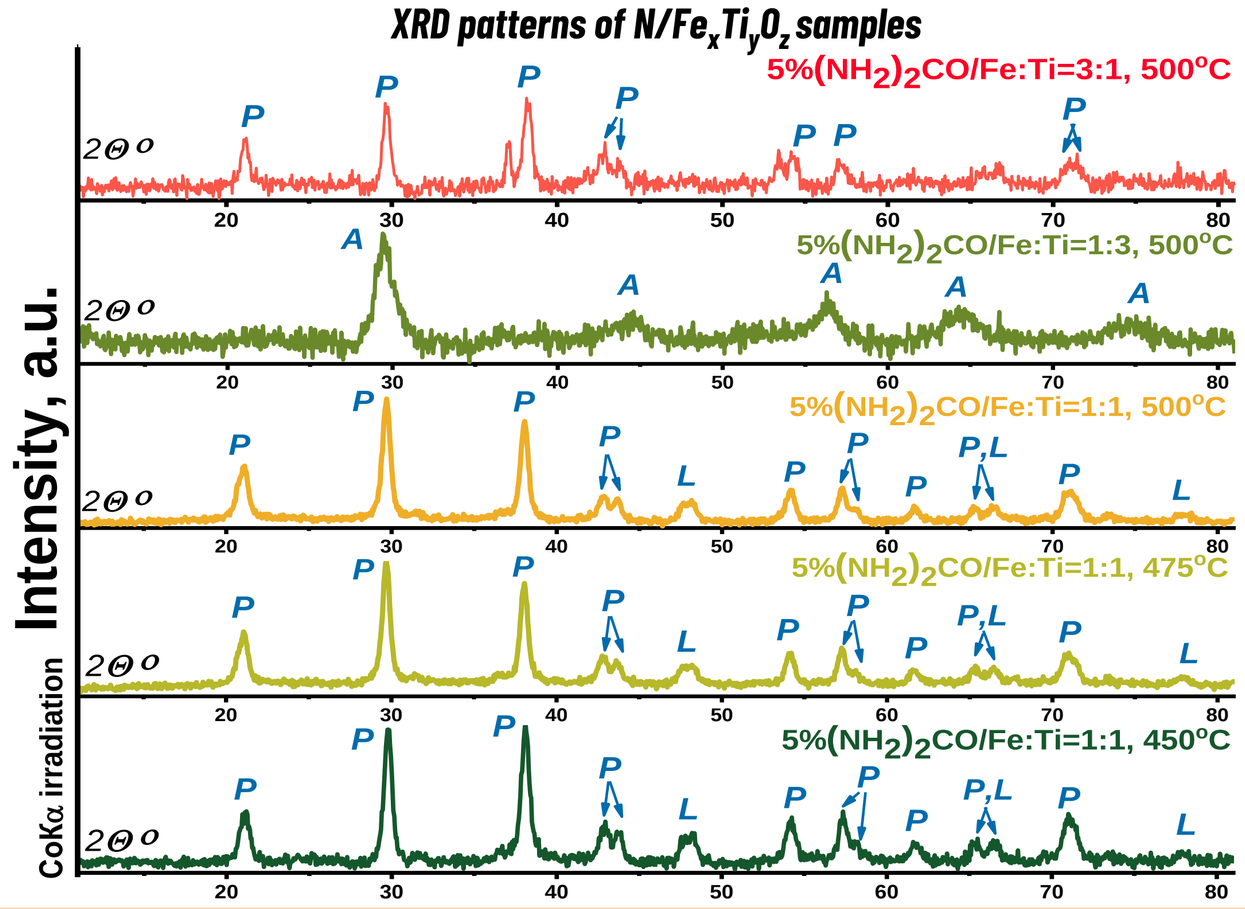
In terms of ecological photocatalysis, semiconductive materials have to satisfy the certain conditions as visible light absorption, non-toxicity, strong resistance to aggressive media and inexpensiveness. Titania is a commonly used photocatalyst in green chemistry application. Incorporation of Fe^{3+} cation in titania lattice depending on the synthesis conditions (heat treatment, iron content) can lead to crystallization of naturally formed phases such as hematite, pseudobrookite, pseudorutile, landauite. The idea of this research is to investigate properties of the thin nanosized photocatalytic films depending on Fe to Ti contents and to determine the factors affecting the crystallization of the obtained phases.

Photocatalysts` synthesis procedure via sol-gel method



XRD observations

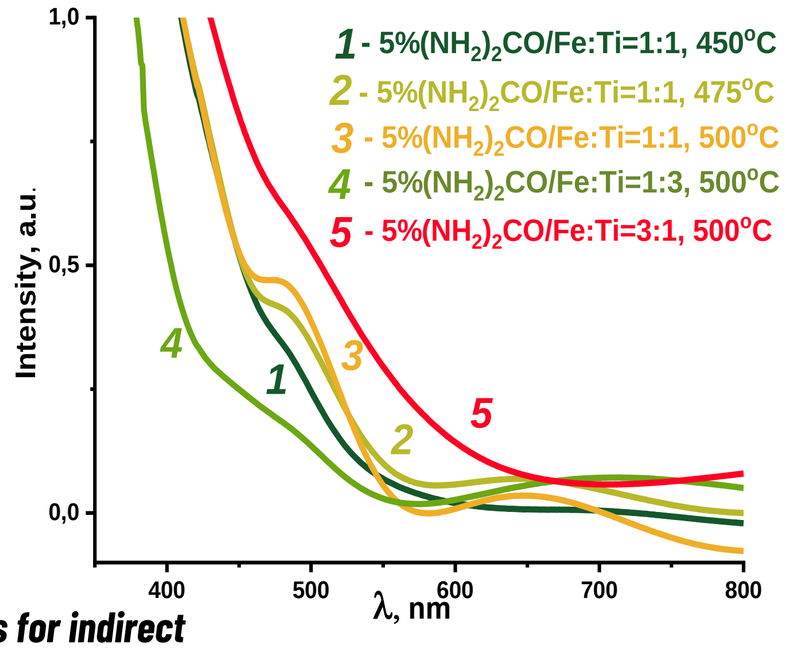


XRD data has shown the formation of Fe_2TiO_5 (*P*-pseudobrookite) and $Fe_2Ti_2O_7$ (*L*-landauite) crystalline phases for all $N/Fe_xTi_yO_z$ samples occurs excepting Fe:Ti=1:3 film where anatase (*A*) is formed. According to the Scherrer equation, the diameter of obtained iron titanates crystallites is in the range from 15 to 18 nm for all Fe:Ti=1:1 and Fe:Ti=3:1 films whereas the lower sized particles (8 nm) of anatase are formed in the structure of Fe:Ti=1:3 sample. It must be noted that the crystallization of pseudobrookite as a main phase can be achieved by changing the metal ions ratio.

Characteristics of $N/Fe_xTi_yO_z$ samples

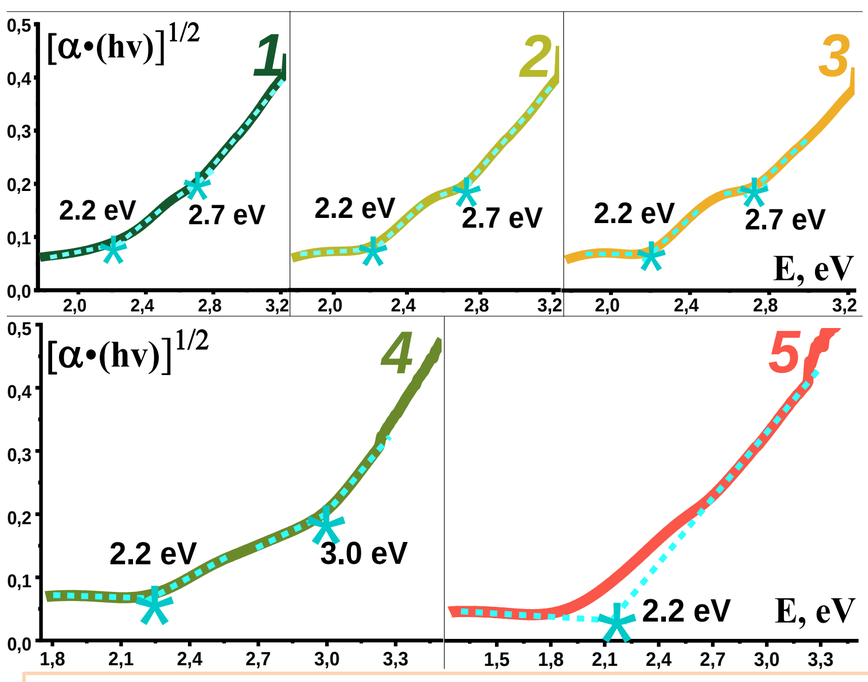
Optical properties

Absorption spectra of $N/Fe_xTi_yO_z$ films



The red shifted onset near 500 nm of the optical band in the absorption spectra of all Fe:Ti=1:1 (450, 475, 500 °C) samples is noted. The Fe:Ti=1:3 and 3:1 films show spectral shift to the shorter (~ 450 nm) and longer (~ 550 nm) wavelength, respectively. It could be noticed that the shift of the optical band onset depends on the Fe to Ti ratio as shown from the spectra.

Tauc plots for indirect transitions and obtained optical band gap values

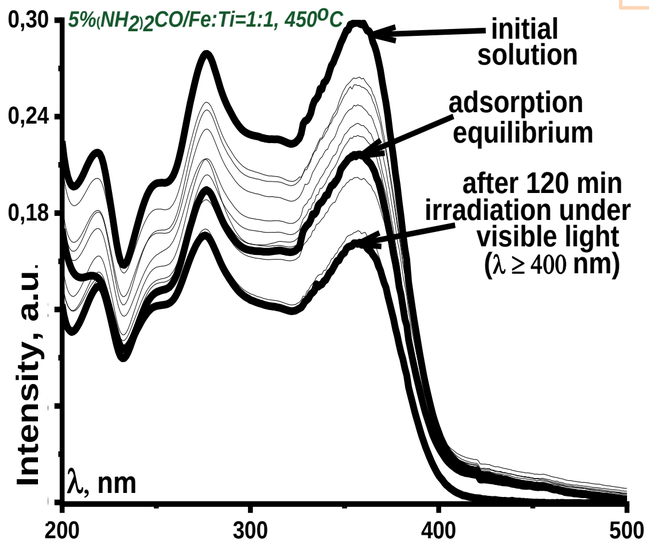


It was calculated the optical band gap energy values for indirect transitions. Two E_g values, 2.2 eV and 2.7 eV, are received for all Fe:Ti=1:1 samples indicating the formation of two phases of iron titanates. It was determined that E_g values of the films with Fe:Ti=1:3 molar ratio are 3.0 eV and 2.2 eV that are attributed to anatase and pseudobrookite ones. In the case of Fe:Ti=3:1 films, the Tauc plot as well as XRD data points on the Fe_2TiO_5 formation with the shoulder in the visible region.

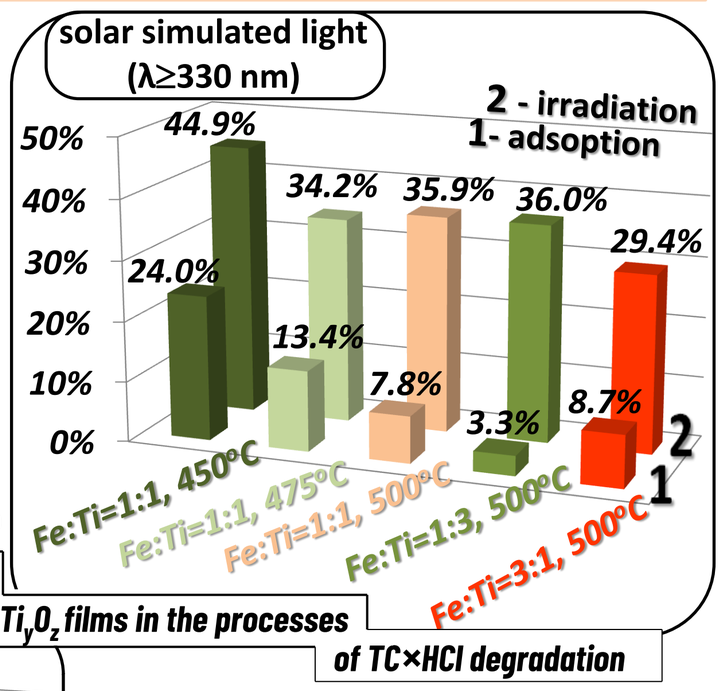
Photocatalytic activity

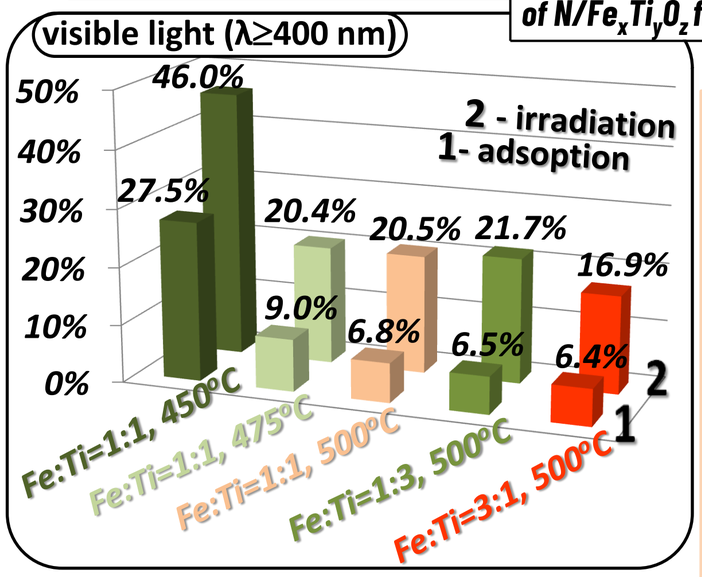
The photocatalytic activity was tested in tetracycline hydrochloride (TC×HCl) destruction as well-known consumed antibiotic in cattle, poultry farming.

Absorption spectra evolution of TC×HCl aq. sol. during visible irradiation over Fe:Ti=1:1 (450 °C) sample



Adsorption level and photocatalytic activity of $N/Fe_xTi_yO_z$ films in the processes of TC×HCl degradation





The highest conversion percentage (46%) as well as the adsorption ability was detected under visible light (λ ≥ 400 nm) for Fe:Ti=1:1 sample annealed at 450°C. Photoactivity of the 1 to 1 ratio films was decreased with calcination temperature increase. The Fe:Ti=1:3 film showed similar activity to Fe:Ti=1:1 (475 °C and 500 °C) samples. However, the last films were more active compare to the Fe:Ti=3:1 under both solar simulated (λ≥330 nm) and visible light irradiation.

Thus, the variation of Ti and Fe contents during sol-gel synthesis of three-layered films as well as the calcination temperature influences on the films composition that, in turns, determines the adsorption capability and photocatalytic activity in the process of tetracycline degradation. As shown by XRD results, the films with the equal content of metals treated at different temperatures are crystallized to the mixture of pseudobrookite and landauite. The three times higher content of Fe compared to Ti ones leads to crystallization of pseudobrookite, whereas anatase formation is detected in the opposite case. Taking into account the metal ions ratios and the stoichiometry of formed phases, the "excess" of iron ions in the structure can be expected for both Fe:Ti=3:1 and Fe:Ti=1:3 samples. Based on analysis on bandgap energy values obtained from Tauc plots, the formation of small particles, undetectable for XRD, of pseudobrookite with Eg=2,2 eV and the incorporation of Fe ions into anatase lattice leading to the decrease of optical Eg to 3.0 eV can be suggested for Fe:Ti=1:3 films. It is proposed that the visible light absorbance (near 500-600 nm) can be attributed to the presence of Fe ions in the structure of Fe:Ti=3:1 films. It is shown that the adsorption of TC molecules on surface of the films plays a crucial role in the photocatalytic efficiency of antibiotics degradation.