FMR and photocatalytic investigations of nNi-TiO_2 (n=1%, 5% and 10%) compounds

N. Guskos[1,2] A. Guskos[2], S. Glenis[1], G. Zolnierkiwicz[2], J. Typek[2], P. Berczynski[2], D. Dolat[3], B. Grzmil[3] , B. Ohtani[4] and A.W. Morawski[3]

[1]Department of Solid State, Faculty of Physics, University of Athens, Panepistimiopolis, Zografou 15 784, Greece

[2]Department of Physics, West Pomeranian University of Technology, Al. Piastow 48, 70-311 Szczecin, Poland

[3]Department of Chemical and Environmental Engineering, West Pomeranian University of Technology, Al. Piastow 17, 70-310 Szczecin, Poland

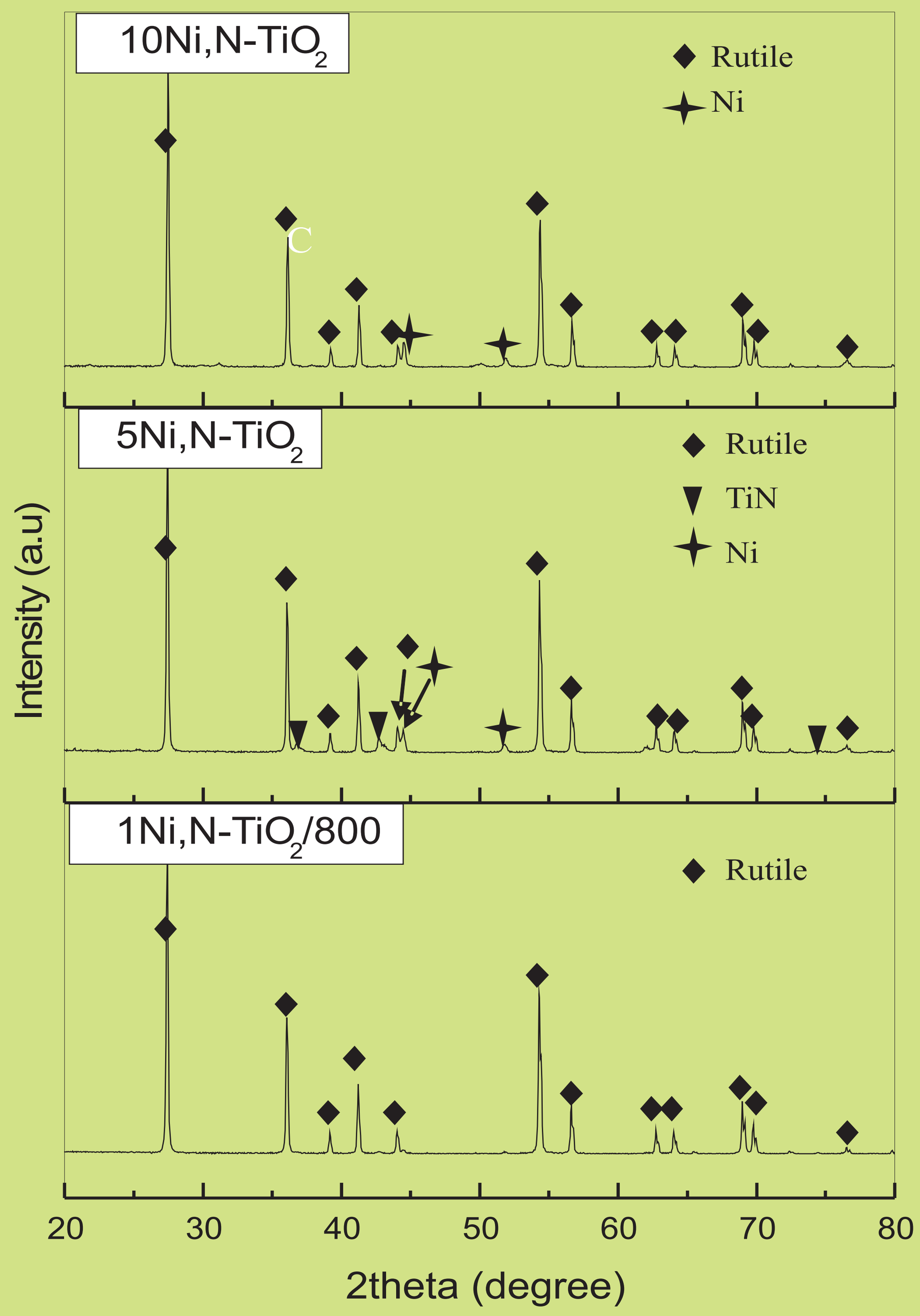
[4]Catalysis Research Center, Hokkaido University, Sapporo 001-0021 Japan

Introduction

Titanium dioxide (TiO_2) is well known as chemically stable and harmless photocatalyst. However, ultraviolet-light irradiation is necessary to fulfill its photocatalytic functions, so TiO_2 photocatalyst holds limitation of application range and effective use of light. In order to improve its photocatalytic efficiency and to expand the application fields, development of visible-light or natural sunlight responsive photocatalyst is demanded. This is done by modifying the surface of the semiconductor and by using transition metals or non-metallic elements doped into TiO_2. Nickel is one of transition elements used to modify the titania surface but Ni doped TiO_2 system is sparsely studied, so information of its physical and chemical properties is needed.

Sample preparation

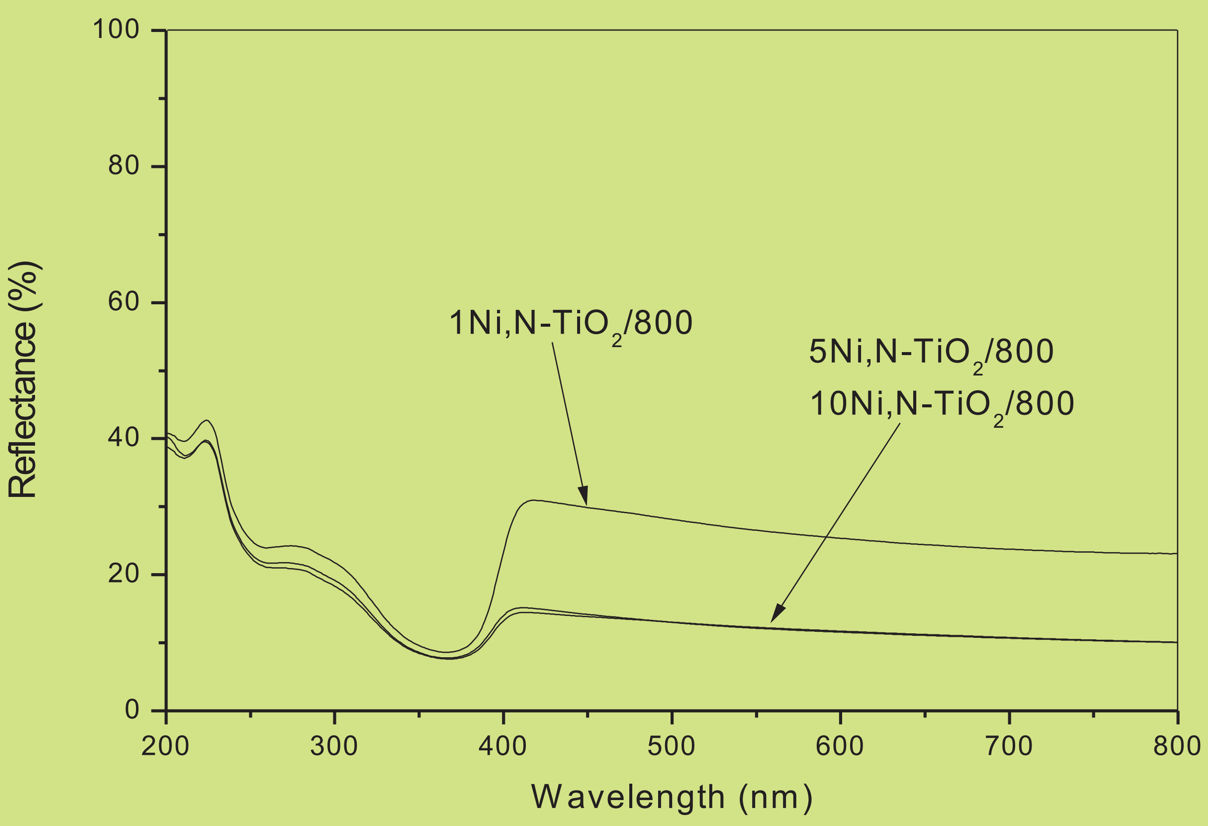
Water suspension of an industrial grade amorphous titanium dioxide (TiO_2/A) from sulfate technology supplied by "Chemical Factory Police S.A." (Poland) was used as a starting material. Commercial TiO_2 P25 (Evonik, Germany) was used for a comparison purpose. About 20 g of TiO_2 water suspension, containing ca. 35 wt.% of titanium dioxide and ca. 8 wt.% of residual sulfuric acid as related to TiO_2 content, was introduced into a beaker containing aqueous solution of $Ni(NO_3)_2$ and stirred for 48 h. The amount of Ni introduced to the beaker was of 1 wt.%, 5 wt.% or 10 wt.% relatively to TiO_2 content. After water evaporation, the samples were dried at 80°C for 24 h in an oven. Subsequently, the material was calcined for 4 hours at 800°C in NH_3 flow.



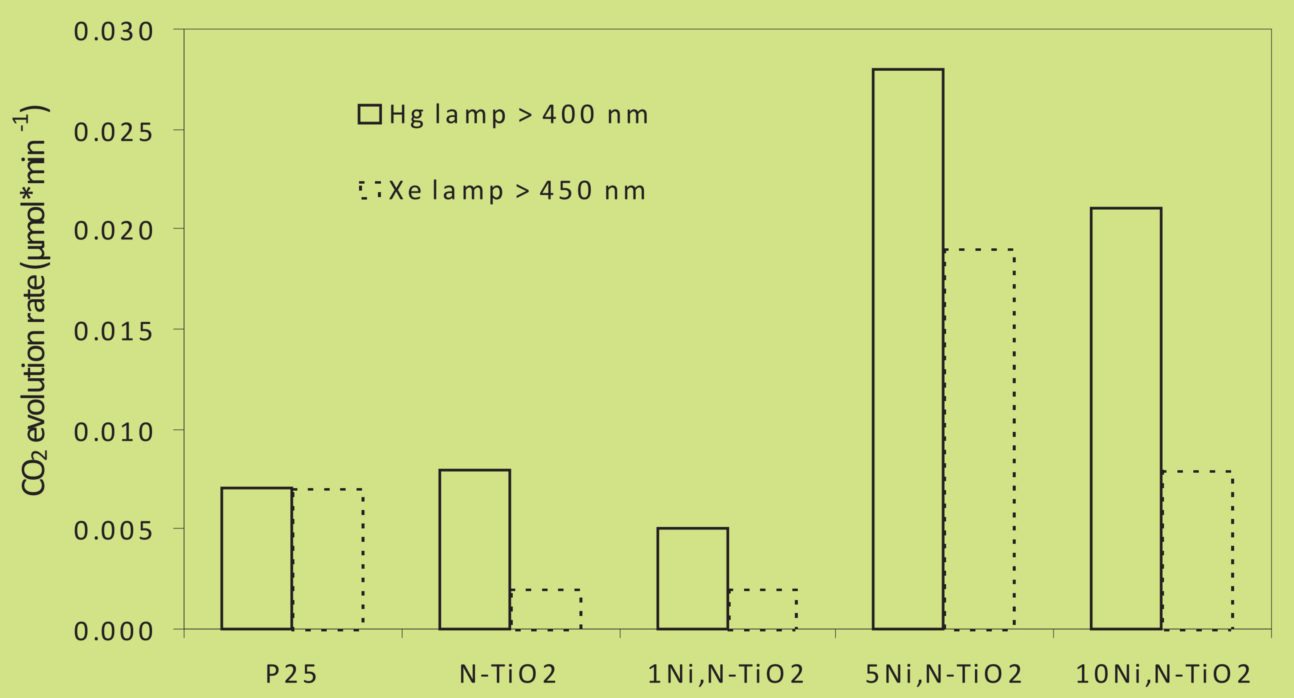
The phase composition of Ni,N-co-modified TiO_2 is rather complex . In case of the sample prepared with 1 wt.% of Ni it is difficult to distinguish any other phase than rutile. Thus, we have assumed that if any other crystalline phase is present in the structure of 1Ni,N-TiO_2 its amount is negligible. In samples 5Ni,N-TiO_2 and 10Ni,N-TiO_2, a metallic nickel was detected. In sample 5Ni,N-TiO_2, besides the metallic nickel, also TiN phase appeared after modification process.

Apparatus

Magnetic resonance spectra were registered on BRUKER E500 X-band (9.4 GHz) spectrometer equipped with Oxford helium flow cryostat enabling measurements in 4-300 K temperature range.



This light absorption increase was significantly higher in case of the co-modified samples, which corresponded to their almost black color, whereas the single-modified samples were yellow. The main reasons for this phenomenon are: the presence of nickel oxides, the doping with nitrogen as well as the lattice defects in the photocatalysts structure.



A high photocatalytic activity of 5Ni,N-TiO_2 sample is caused by the following factors: a) rutile form of TiO_2, which assures better stability and light absorption ability than anatase or amorphous TiO_2; b) doped nitrogen in the photocatalyst structure, mainly in the bulk of TiO_2, which allows visible light absorption by narrowing the band-gap of the material; c) the presence of Ti^{3+} ions in the bulk of the photocatalyst in amount which increases the visible light absorption, additionally increasing TiO_2 stability but does not yet serve as hole trap and therefore does not inhibit the photocurrent; d) nickel modification, resulting in significant amounts of nickel on the photocatalysts surface as well as in the bulk; e) the presence of TiN on its surface, which may also serve as an electron trap and increase the charge separation

The Callen-lineshape

$$I(H) \quad \frac{H_0^2 \; H_0^2 \quad {}^2_B \; H^2 \quad {}_B \quad 2H_0|H| \quad {}_B \quad H_0^2 \; H_0^2 \quad {}^2_B \quad {}_B}{H \quad H_0{}^2 H_0^2 \quad |H| \quad {}_B \quad H_0 \; {}_B{}^2 \quad H \quad H_0{}^2 H_0^2 \quad |H| \quad {}_B \quad H_0 \; {}_B{}^2}$$

where H_0 is the true resonance field, Δ_H is the true linewidth connected with relaxation of the Landau-Lifshitz type, and δ_H a true linewidth connected with relaxation of the Bloch-Bloembergen type.