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Recharge processes of paramagnetic centers during illumination in nitrogen-doped nanocrystalline titanium dioxide

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ABSTRACT

Nitrogen-doped titanium dioxide (N-TiO_2) has been investigated by the EPR-technique. Two types of paramagnetic centers – $N^\bullet$ and $NO^\bullet$-radicals – were detected in the samples. Both $N^\bullet$ and $NO^\bullet$-related centers are recharged during illumination. Band diagrams of TiO_2 with $N^\bullet$ and $NO^\bullet$ radicals energy level position are proposed.

1. Introduction

Less than a decade ago, the physical-chemical properties of nanocrystalline titanium dioxide (TiO_2) and especially nitrogen-doped titania were intensively studied for TiO_2-based device development, intended for air and water purification via surface photocatalytic reactions using the visible light spectrum [1–4]. A unique and very important (especially for photocatalytic application) property of TiO_2 is a large specific surface area of about 100 m^2/g [5]. It provides the possibility of an effective interaction of TiO_2 nanocrystal with molecules at the surface, with a great impact on its physical–chemical properties [1,5,6], leading to a generation of a high concentration of oxygen related radicals at the TiO_2 surface [3,5,6]. These radicals are responsible for air and water purification [5,7]. Doping the TiO_2 structure with different elements and, particularly, with nitrogen, leads to the presence of local energy levels in the band gap of TiO_2 [3,5,6]. This material becomes photosensitive in the visible range of spectrum because of the absorption of light by the impurities [3,5–7]. A decade or more ago titania was also doped with different transition metal ions [8,9], sulfur [10], carbon [11,12]. Unfortunately, these elements (impurities) have a low solubility in titania and the photocatalytic properties of such samples degraded with time owing to a diffusion of impurity atoms to the surface following oxidation with the oxygen from the environment [5]. Nitrogen-doped TiO_2 samples are free from such shortcomings and have persistent photocatalytic properties [7,13,14].

The goal of this work is to study the influence of dopant content on the radical concentration and processes of paramagnetic center (PC) recharge under illumination in the nitrogen-doped nanocrystalline titanium dioxide. In the present work we have used, for the first time, EPR spectroscopy and optical excitation in a wide range of quantum energies for the evaluation of the dopant related level position with respect to the bottom of the conduction band in nitrogen-doped titania.

2. Experimental results and discussions

The sol–gel method was used to generate titanium dioxide. Titanium (IV) isopropoxide (TIP), Fluka analytical, and isopropanol extra pure, Accros organics, were used as purchased. 9.6 mL TIP was added to 10 mL isopropanol. Reaction was achieved by adding 10 mL of ultrapure water Milli-Q at room temperature. The sol–gel product was washed with pure water, filtered, and dried overnight at 70 °C. The powder was then annealed in air at 450 °C for 1 h with the ramp of 5 °C/min. To prepare the N-doped titanium dioxide, we proceeded by adding a solution of ammonium to the isopropanol/TIP solution instead of pure water. The mass ratio N:Ti calculated with the initial amount of nitrogen and titanium was 1.87% for N-doped samples. This final product is named $TiO_{2-x}N_x$ sol–gel. The samples with different N/Ti ratio are named: sample a0 (N/Ti = 0), sample a1 (N/Ti = 1.9), sample a2 (N/Ti = 3.7), sample a3 (N/Ti = 5.6).

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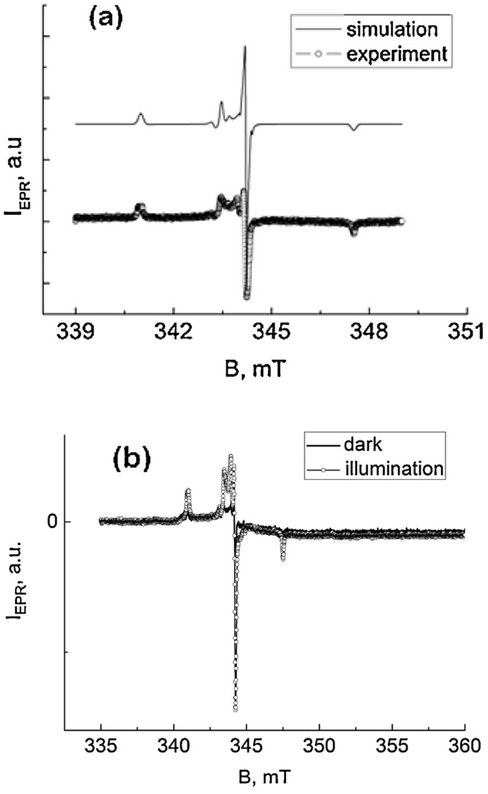

Figure 1. (a) EPR spectra of a2 samples: experiment and simulation. $T = 300$ K. (b) EPR spectra of a2 samples in dark and under illumination by tungsten lamp. $T = 300$ K.

EPR spectra were detected by the standard Bruker EPR spectrometer ELEXSYS-500 (X-band, sensitivity is around $\sim 10^{10}$ spin/G). To illuminate the samples directly in the spectrometer cavity, the optical cavity was used. The samples were positioned in flat ampoules. Etalon $CuCl_2 \cdot 2H_2O$ was used for the calculation of paramagnetic center (PC) concentration. The samples were illuminated in situ with high pressure tungsten lamp in the spectral range 400–1000 nm, and with a monochromatic illumination with wavelengths: 750, 700, 650, 600, 550, 500, 450, 400, 350 nm (or quantum energies: 1.7, 1.8, 1.9, 2.1, 2.3, 2.5, 2.8, 3.1, 3.6 eV, respectively). The selection of wavelengths (quantum energies) was performed by the monochromator MDR-204. The intensity of the illumination was 40 mW/cm^2. The kinetics of the EPR signal intensity relaxation were detected at the value of a magnetic field equal to that of the resonance, using a special option of the EPR spectrometer ELEXSYS-500: the x-coordinate is the time axis, and the y-coordinate is the EPR signal intensity axis. The measured temperature was 300 and 77 K. Experiments at liquid nitrogen temperature were made using Bruker ER4112HV temperature control system.

All N-doped samples are characterized by EPR. As example, the EPR spectrum of a2 sample measured at 300 K is represented in Figure 1a and b.

The simulation of these experimental data was performed in EASYSPIN© Program. The result is also shown in Figure 1a. The simulation parameters were as follows: the g-tensor – $g_1 = 2.00845$, $g_2 = 2.00405$, $g_3 = 2.00385$; the width of EPR line – $\Delta H_1 = 1.44$ G, $\Delta H_2 = 0.4$ G, $\Delta H_3 = 2.3$ G and the hyperfine interaction constants – $A_1 = 1.54$ G, $A_2 = 1.09$ G, $A_3 = 21.8$ G.

The EPR signal with such parameters according to our, and literature data, can be attributed to paramagnetic centers type as nitrogen atoms (nuclear spin $I = 1$) with uncompensated electron spin embedded into TiO_2 matrix while preparing the samples [15,16]. N-atoms in TiO_2 matrix could be either O-substitutional (Ti–N•–Ti) or interstitial (O–N•–Ti) [16]. The intensity of EPR signal increases under illumination (Figure 1b). Therefore one could suppose the existence of nitrogen atoms in a charged diamagnetic state N^- along with N^0 paramagnetic centers in N-TiO_2. The latter could be realized under the condition of electron transition from Ti^{3+}/oxygen vacancy centers to interstitial nitrogen atoms. Hence Ti^{3+}-centers transfer to Ti^{4+}-centers in nitrogen-doped TiO_2 samples.

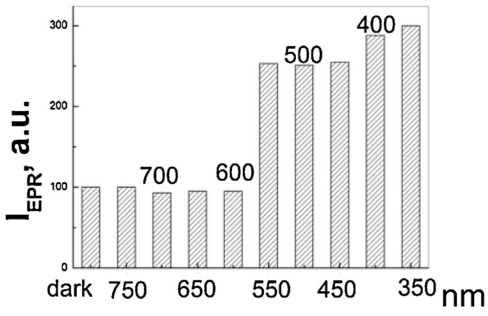

Figure 2. EPR signal intensity of N•-radicals versus the wavelength of irradiation. $T = 300$ K.

To estimate a location of N-related PC energy levels in the band gap, we have investigated the dependence of EPR signal intensity with the wavelength of light. The results of different wavelength illumination of N-related PC are shown in Figure 2. Notice that, as follows from Figure 2, only with a definite wavelength (quantum energy) there is a change of intensity of the EPR signal.

The effect of illumination was reversible during approximately one minute supporting the recharged processes of radicals in TiO_2 nanocrystals in dark–illumination–dark cycle. To understand the dynamics of these processes we have studied a relaxation of EPR signal intensity after switching off the illumination. Figure 3 shows the experimental kinetics of the EPR signal relaxation and its fitting by two exponents with $\tau_1 = 33$ s (fast decay) and $\tau_2 = 815$ s (slow decay). The evidence that the curve consists of two different parts points out to the existence of two processes in the samples under investigation. We believe that the two-time constant EPR signal relaxations can be explained by a recharge of two types of the N-related centers. As it was noted above, such centers can be O-substitutional or interstitial N-atoms in TiO_2 matrix.

An N-related impurity absorption of the light in the investigated samples leads to recharging the N-related centers: $N^- + h\nu \rightarrow N^0$ (N• radical) + e^- (in the conduction band). Threshold of EPR signal intensity for N• radicals was 550 nm (2.2 eV) see Figure 2. Therefore we can assume that position of N-related level in the band gap is 2.2 eV, see Figure 4.

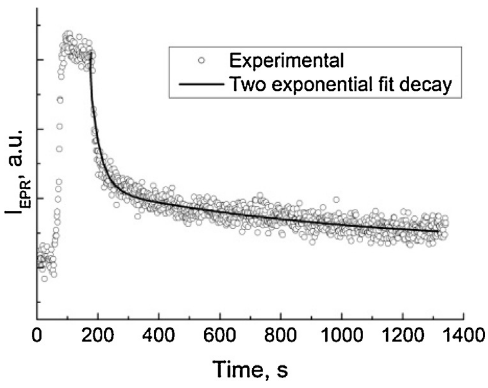

Figure 3. Experimental kinetic of EPR signal relaxation for a2 sample and its fit by two exponent.