Effect of Nb doping on the hydrophilicity of TiO$_2$ thin films

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Motivation

Self-cleaning coatings have considerable attention for both their unique properties and practical applications in energy and environmental areas. Since the effect of surface photoinduced superhydrophilicity was discovered in 1997 (Fig. 1) the TiO$_2$ based photocatalysts have gained considerable attention [1].
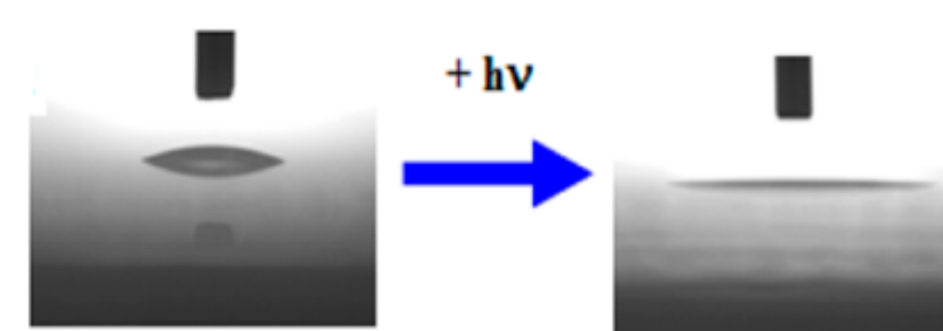
Fig. 1. TiO$_2$ nano-coating: UV-induced superhydrophilic conversion

Strategy to improve the efficiency of photocatalytic and self-cleaning properties is described in detail elsewhere [2]. Here we studied the effect of metal doping on the wettability of TiO$_2$ thin films, using niobium ion Nb^{5+} as example.

Synthesis and Characterization

The x-Nb-TiO$_2$ films (x: 0, 0.2, 0.4, 0.6, 0.8, 1.0 at.%) were prepared on glass and conductive (FTO) supports by dip-coating method from Nb-TiO$_2$ sols with following annealing at 480ºC for 8 hours. x-Nb-TiO$_2$ powders were precipitated from corresponding x-Nb-TiO$_2$ sols.
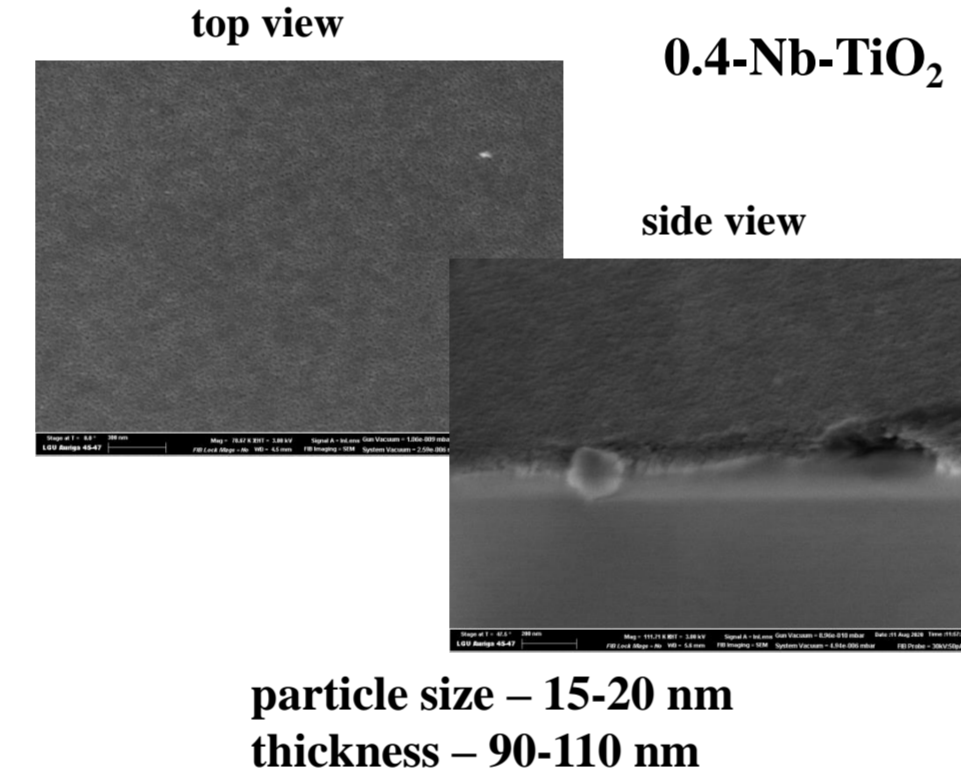
XRD: anatase

r(Nb^{5+}) ~ r(Ti^{4+})
r(Ti^{4+}) = 0.605 Å
r(Nb^{5+}) = 0.680 Å
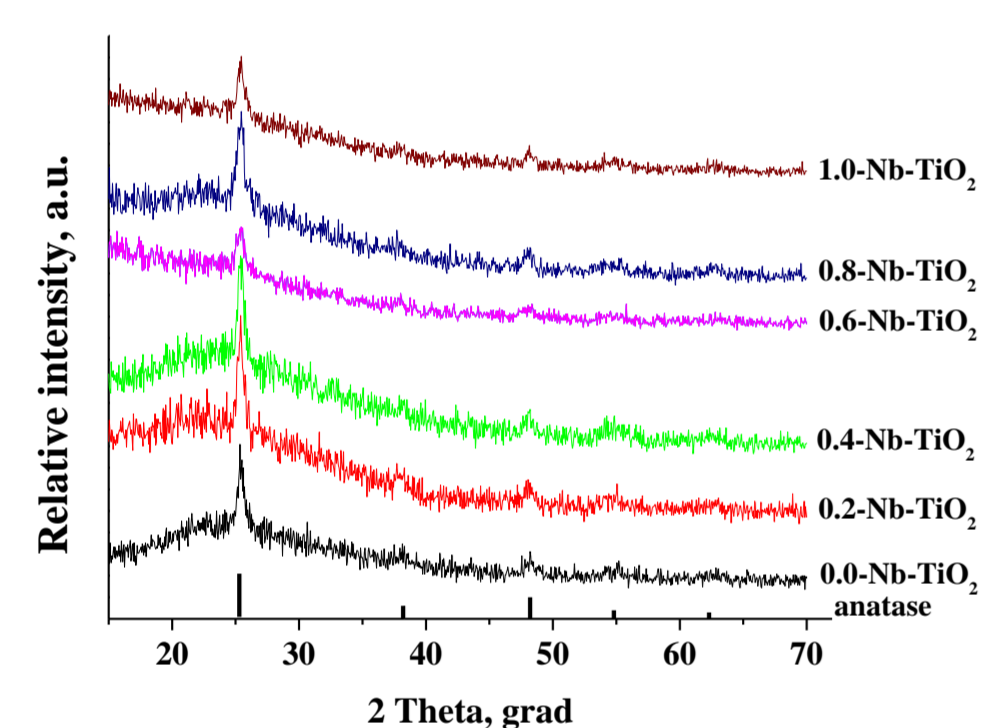
With the dopant content increasing, the micro-strain in the film samples does not change significantly.
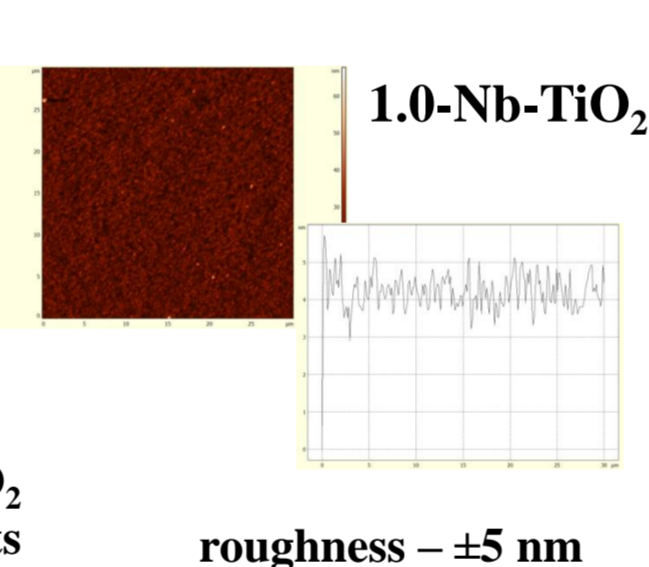
SEM

0.4-Nb-TiO$_2$
top view
side view
particle size – 15-20 nm
thickness – 90-110 nm

XPS and EDX data

Sample	[Nb^{5+}] on surface, at.%*	[Nb^{5+}] in bulk, at.%**
0-Nb-TiO$_2$	0.0	0.0
0.2-Nb-TiO$_2$	0.21	0.22
0.4-Nb-TiO$_2$	0.39	0.38
0.6-Nb-TiO$_2$	0.51	0.64
0.8-Nb-TiO$_2$	0.65	0.81
1.0-Nb-TiO$_2$	0.83	1.08

* XPS, ** EDX

The Nb content on the TiO$_2$ surface becomes lower than its total content in the bulk starting from concentrations >0.6 at.%.

AFM

1.0-Nb-TiO$_2$
roughness – ±5 nm

FT-IR spectra of x-Nb-TiO$_2$ samples: OH stretching region

0.0-Nb-TiO$_2$
0.2-Nb-TiO$_2$
0.4-Nb-TiO$_2$
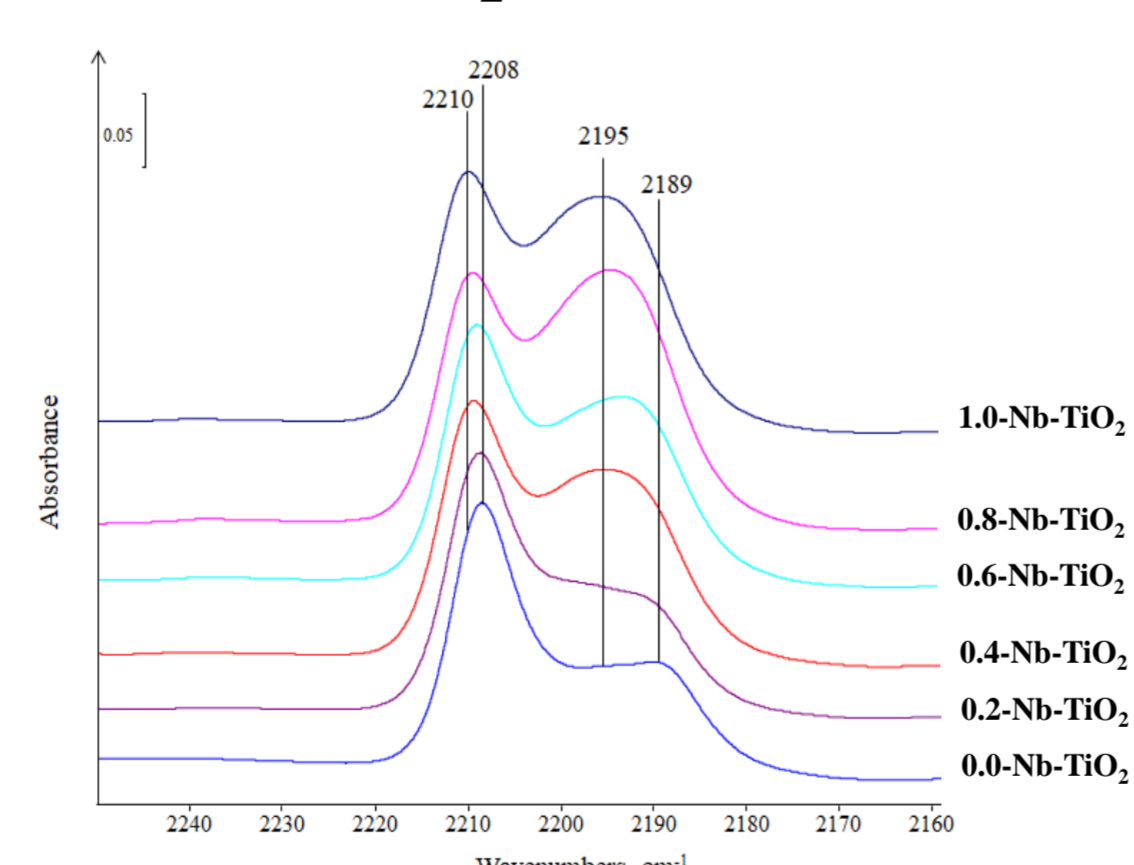0.6-Nb-TiO$_2$
0.8-Nb-TiO$_2$
1.0-Nb-TiO$_2$
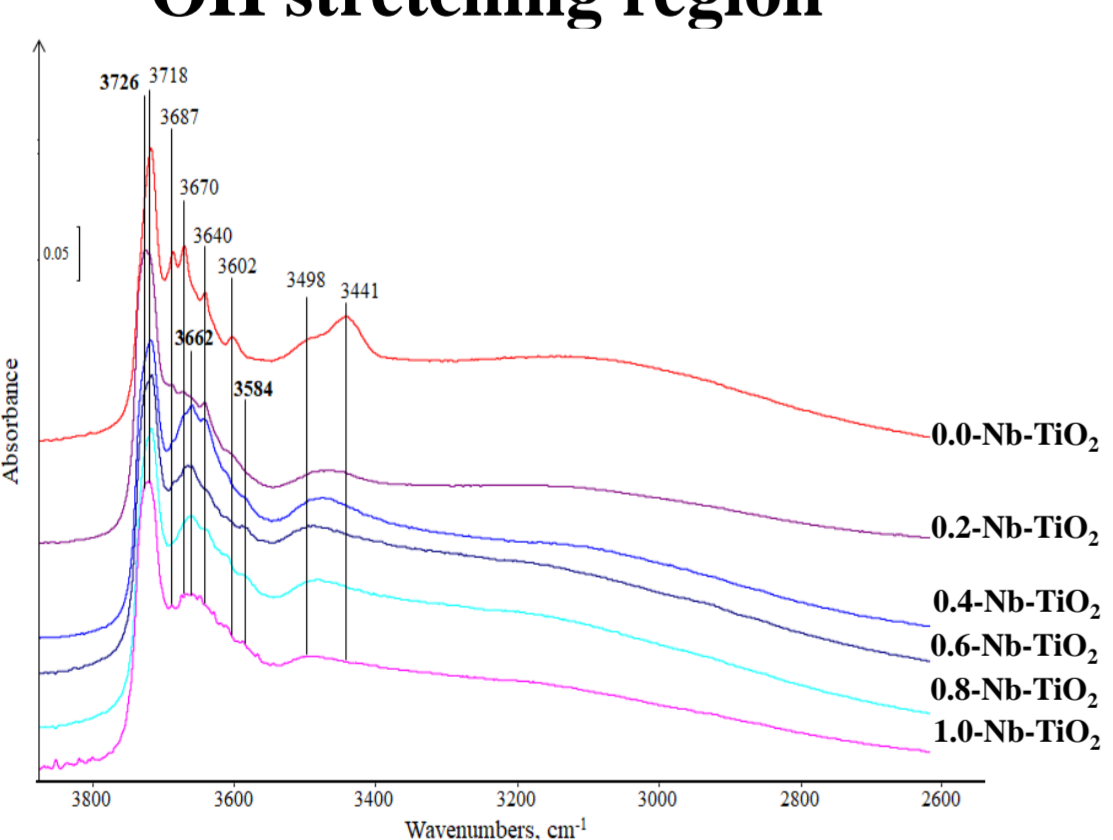
With Nb dopant increasing:
- the formation of new isolated OH groups (3726 cm^{-1} as a shoulder)
- the formation of new bridging OH groups (bands at 3662 cm^{-1} and 3584 cm^{-1})

FT-IR spectra of CO adsorbed on x-Nb-TiO$_2$ surfaces at 300 K

1.0-Nb-TiO$_2$
0.8-Nb-TiO$_2$
0.6-Nb-TiO$_2$
0.4-Nb-TiO$_2$
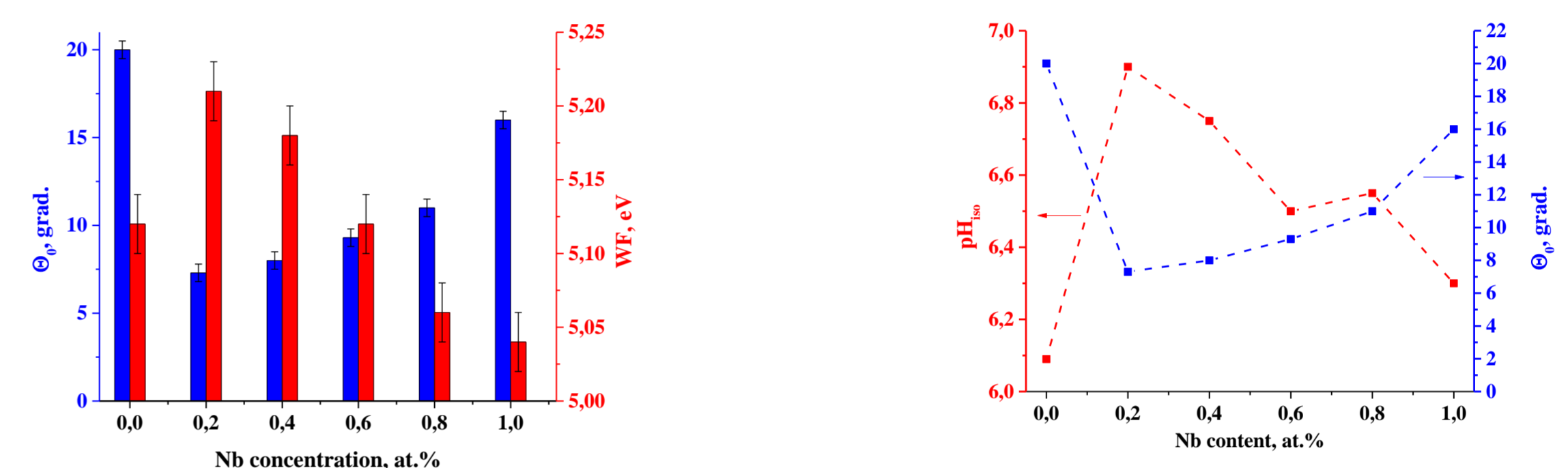0.2-Nb-TiO$_2$
0.0-Nb-TiO$_2$

The appearance of the band at 2195 cm^{-1} and band-shift from 2208 cm^{-1} to 2210 cm^{-1} indicate an increase in the acidic strength of the Lewis sites on the surface with Nb dopant increasing.

Self-supported powder pellets were preliminary dehydrated at 450ºC. IR spectra were registered at room temperature with spectral resolution of 4 cm^{-1}.

Wettability of x-Nb-TiO$_2$ Surfaces

Dependences of initial water contact angle values (Θ_0), work function values (WF), surface acidity (pH$_{iso}$) and surface free energy (SFE) on Nb dopant concentration

Sample	Θ_0,[1] grad.	WF,[2] eV	pH$_{iso}$[3]	SFE, mN/m[4] t	d	p
0-Nb-TiO$_2$	20.0 ± 0.5	5.12 ± 0.02	6.09 ± 0.05	75.9 ± 0.5	47.8 ± 0.4	28.1 ± 0.2
0.2-Nb-TiO$_2$	7.5 ± 0.5	5.21 ± 0.02	6.90 ± 0.05	79.5 ± 0.5	48.2 ± 0.4	31.3 ± 0.2
0.4-Nb-TiO$_2$	8.0 ± 0.5	5.18 ± 0.02	6.75 ± 0.05	79.3 ± 0.5	48.2 ± 0.4	31.1 ± 0.2
0.6-Nb-TiO$_2$	9.5 ± 0.5	5.12 ± 0.02	6.50 ± 0.05	79.4 ± 0.5	48.2 ± 0.4	31.2 ± 0.2
0.8-Nb-TiO$_2$	11.0 ± 0.5	5.06 ± 0.02	6.55 ± 0.05	78.8 ± 0.5	47.1 ± 0.4	31.7 ± 0.2
1.0-Nb-TiO$_2$	16.0 ± 0.5	5.04 ± 0.02	6.30 ± 0.05	76.6 ± 0.5	45.1 ± 0.4	31.5 ± 0.2

[1] optical tensiometry, [2] Kelvin probe method, [3] pH-metry [3], [4] SFE$_t$ – total SFE, SFE$_d$ – dispersive SFE, SFE$_p$ – polar SFE, two-liquid method (H$_2$O contact angle *vs.* CH$_2$I$_2$ contact angle), OWRK/Fowkes approach [4]

The work function value increases sharply for the 0.2-Nb-TiO$_2$ sample as compared to that for the undoped sample. At the same time, there is a noticeable decrease in the water contact angle Θ_0. Following increase in the dopant concentration up to 1.0 at.% leads to a gradual decrease in the function work while the Θ_0 value increases.

When doping TiO$_2$, the total SFE$_t$ mostly increases due to its polar component SFE$_p$, but further decrease in the total SFE$_t$ with increasing Nb content occurs due to its dispersive component SFE$_d$, especially pronounced at Nb concentrations above 0.6 at.%.
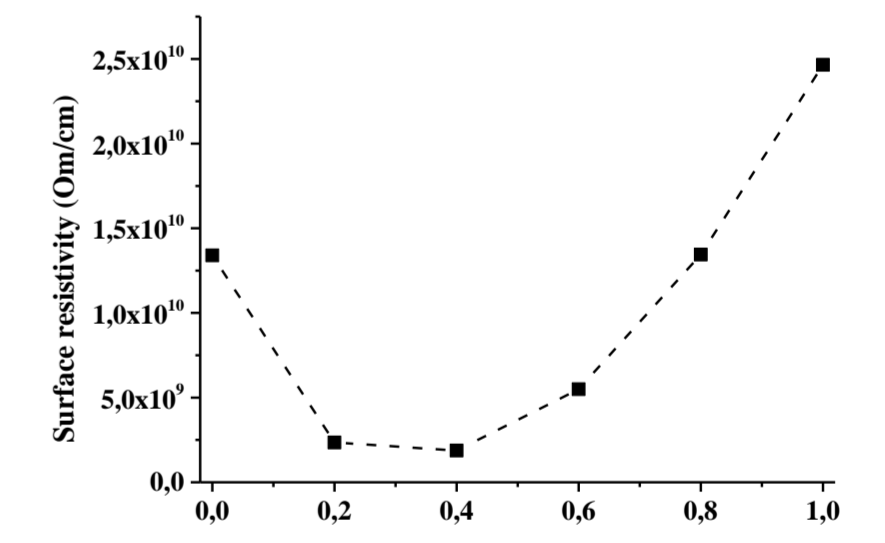
Photoinduced Hydrophilicity
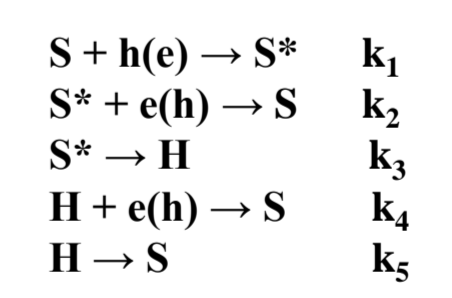
Kinetic dependences of photoinduced WCA alteration

- 0-Nb-TiO$_2$ (1)
- 0.2-Nb-TiO$_2$ (2)
- 0.4-Nb-TiO$_2$ (3)
- 0.6-Nb-TiO$_2$ (4)
- 0.8-Nb-TiO$_2$ (5)
- 1.0-Nb-TiO$_2$ (6)
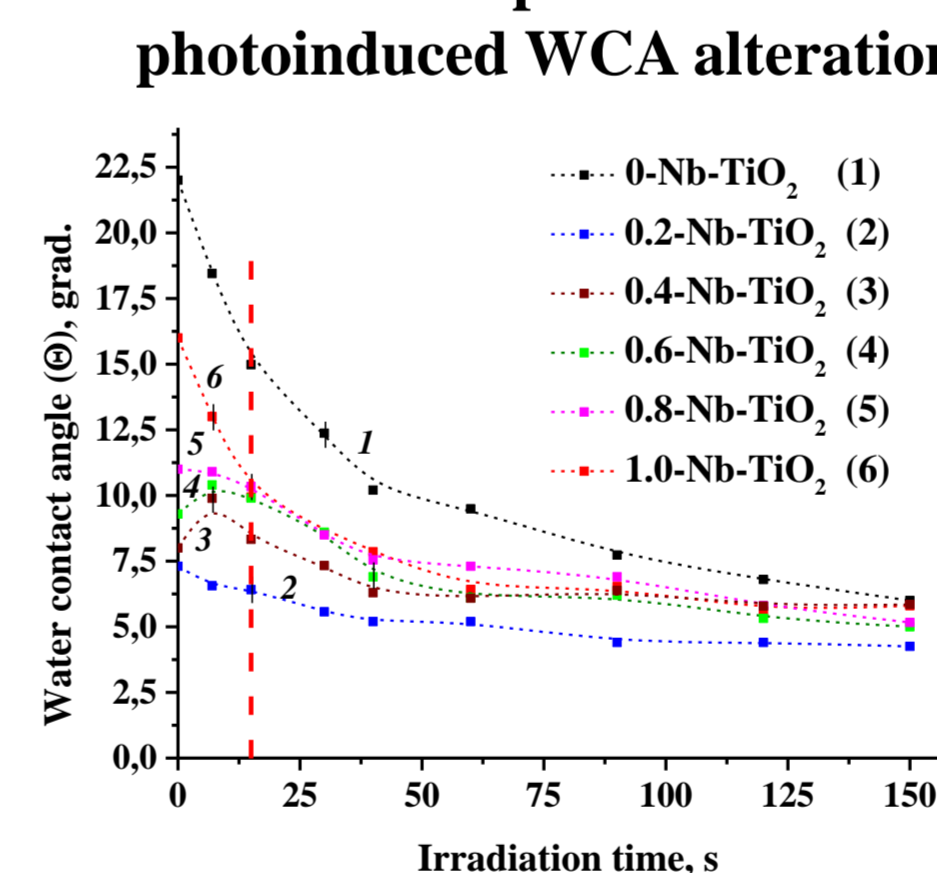
The sample was irradiated using a Hg lamp with a water filter and a UFS-2 filter (irradiance at 365 nm was 0.5 mW/cm^2)

Mitsubishi Hiresta Up MCP HT450 surface resistance meter, two-wire scheme, UA contacts 2 mm in diameter, distance - 20 mm, applied force 240 g), applied voltage 250 V

Sample	Θ_r,[1] grad.	SFE, mN/m initial t	after UV irradiation for 150 s t	d	p
0-Nb-TiO$_2$	6.8 ± 0.5	75.9 ± 0.5	80.4 ± 0.5	48.8 ± 0.4	31.6 ± 0.2
0.2-Nb-TiO$_2$	4.0 ± 0.5	79.5 ± 0.5	80.5 ± 0.5	49.3 ± 0.4	31.2 ± 0.2
0.4-Nb-TiO$_2$	5.8 ± 0.5	79.3 ± 0.5	80.6 ± 0.5	48.5 ± 0.4	32.1 ± 0.2
0.6-Nb-TiO$_2$	5.3 ± 0.5	79.4 ± 0.5	80.7 ± 0.5	48.8 ± 0.4	31.9 ± 0.2
0.8-Nb-TiO$_2$	5.8 ± 0.5	78.8 ± 0.5	80.4 ± 0.5	49.2 ± 0.4	31.2 ± 0.2
1.0-Nb-TiO$_2$	5.8 ± 0.5	76.6 ± 0.5	80.5 ± 0.5	49.5 ± 0.4	31.0 ± 0.2

[1] Θ_r – water contact angle after 150 s-UV irradiation

$$S + h(e) \rightarrow S^* \quad k_1$$
$$S^* + e(h) \rightarrow S \quad k_2$$
$$S^* \rightarrow H \quad k_3$$
$$H + e(h) \rightarrow S \quad k_4$$
$$H \rightarrow S \quad k_5$$

$$\Delta H(t)=H(t)-H_0=[(A/B) S_0 - H_0][1-e^{-(C/B)t}]$$

$A = k_1 \cdot k_3 \cdot n_1$, $B = k_2 \cdot n_2 + k_3$,
$C = k_1 \cdot k_3 \cdot n_1 + k_2 \cdot k_4 \cdot n_2^2 - k_3 \cdot k_4 \cdot n_2$
k_i - the rate constant of the i-th stage
S_0 - the initial concentration of the surface sites (S) acting as either hole or electron trap
n_1 and n_2 - the surface concentrations of the photo-carriers (electrons and holes), participating in activation and deactivation of the active surface sites

Conclusions

A series of Nb-doped films were prepared with niobium content from 0.0 to 1.0 at.%. The chemical and phase composition and surface morphology of the synthesized films were characterized by XRD, XPS, AFM, EDX and SEM methods. No additional micro-strain was detected in the doped films compared to the undoped film.

The Nb doping affects the SFE and hydrophilicity of the film surface as well as surface acidity and the work function (including Fermi level) of x-Nb-TiO$_2$. The acidity of films' surfaces was evaluated by pH-metry method and IR spectroscopic study of CO adsorption. With Nb dopant content increasing, Lewis acidity of the x-Nb-TiO$_2$ surface increases while Brønsted acidity decreases. The work function values deal with electron concentration on the surface as well as the composition of the hydroxyl-hydrated layer.

Photoexcitation of x-Nb-TiO$_2$ in the TiO$_2$ intrinsic absorption region leads to the superhydrophilicity for all films. However, the sign and magnitude of the initial photoinduced hydrophilic/hydrophobic conversion rate at irradiation for seconds correlate with the surface resistivity: the lower the surface resistivity, the greater the positive rate value. For Nb concentrations >0.8 at.%, the highest rate of photoinduced hydrophilic conversion is observed. This is explained by low value of the work function and high concentration of holes on the surface.

References

[1] R. Wang, K. Hashimoto, A. Fujishima, *et al.*, Nature 388 (1997) 431. doi: 10.1038/41233
[2] A.V. Rudakova, A.V. Emeline, Colloid J. 83 (2021), 20. doi: 10.1134/S1061933X21010105
[3] G.A. Parks, P.L. de Bruyn, J. Phys. Chem. 66 (1962), 967–973. doi: 10.1021/j100812a002
[4] D.K. Owens, R.C. Wendt, J. Appl. Polym. Sci. 13 (1969), 1741–1747. doi:10.1002/app.1969.070130815