Phenothiazine Dye Interaction with the Surface of Nanocrystalline TiO_2: FTIR and Raman Spectroscopy Study

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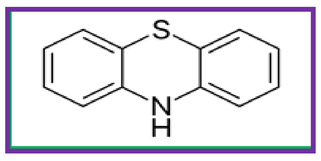
We report on TiO_2 doping with phenothiazine (PTZ) (5% mas.) as an alternative approach to engineering a nonstoichiometric TiO_2 material. There is a great interest in hybrid TiO_2 structures activated with organic dyes. PTZ showing strong electron-donating ability could act as electron donor for TiO_2 known as good electron-acceptor material. In this project we investigated the interaction of organic dye phenothiazine with active surface sites of titanium dioxide particles (anatase and rutile) and studied the effect of dye-sensitization of TiO2 on its structural and optical properties. The analysis of the mechanisms of chemical interaction of PTZ with the TiO_2 surface, which are still not fully understood, is an important task.

Table 1. Characteristics of TiO2 and TiO2/PTZ samples

Samples	Crystal structure	Processing Temperature, ° C	Average crystallite size* (±3nm), nm	Stoichiometry TiO2 O/Ti** (±0.001)	Stoichiometry TiO2/PTZ O/Ti** (±0.001)	BET, m2/g
A1	Anatase	300	10	1.985	1.959	240
R1	Rutile	300	17	2.000	1.994	95
R2	Rutile	900	80	2.000	1.998	3

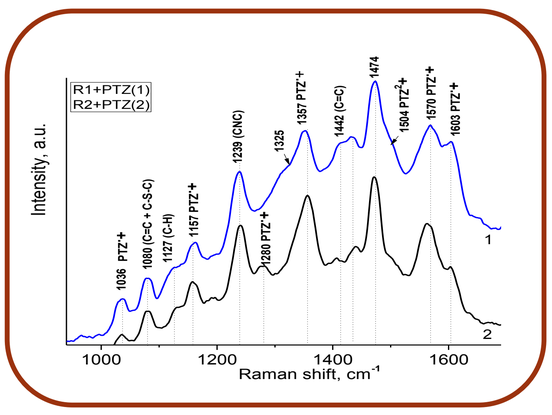
Schematic structure of phenothiazine (C12H9NS)



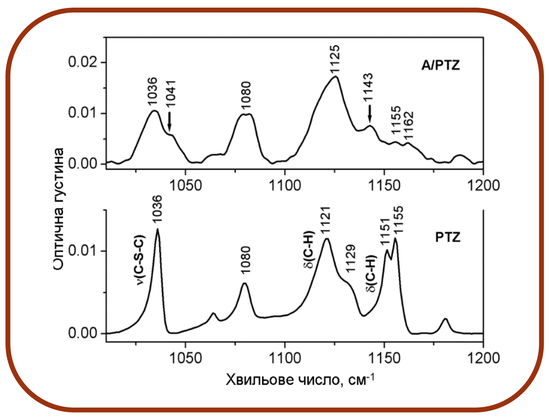
Visual appearance of TiO2/PTZ samples

The experiments have shown that mixing of TiO_2 and PTZ results in a dark-blue color of TiO_2/PTZ. The admixture of PTZ in A/TiO_2 causes a noticeable red shift of TiO_2 absorption edge and narrowing of the band gap both for direct and indirect electronic transitions.

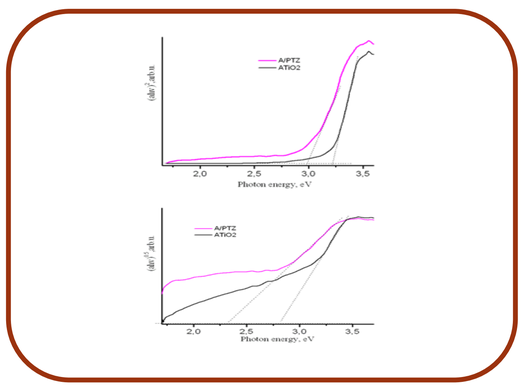
Raman spectra of R300/PTZ and R900/PTZ



Raman spectra of A/PTZ and PTZ

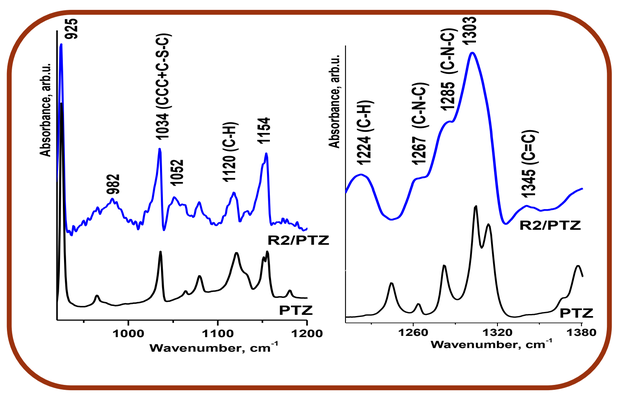


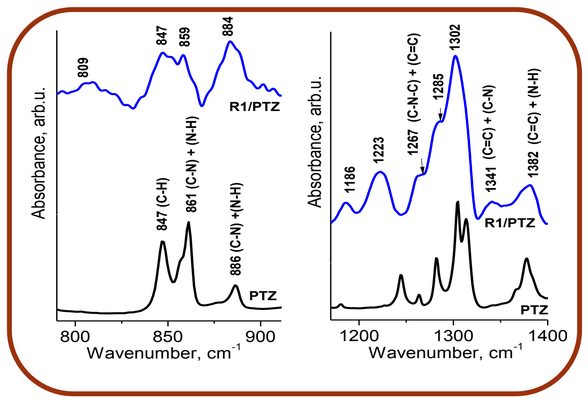
Direct and indirect band gap for A/TiO_2 and A/PTZ



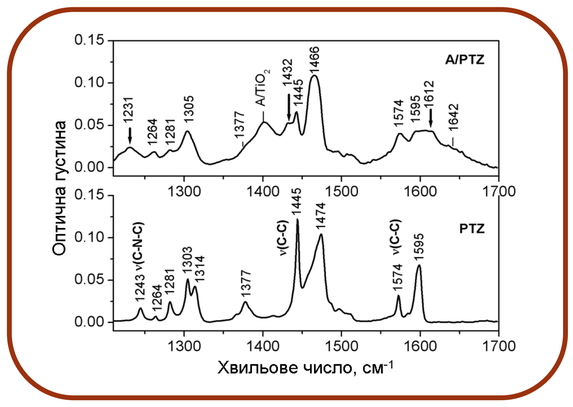
During PTZ adsorption on TiO_2 surface the intensity of the OH-stretching vibrations decreases, which indicates that some part of the OH groups (physisorbed H_2O) is displaced by PTZ molecules from the TiO_2 surface. The other part of the OH groups participates in the formation of the adsorption complex with PTZ molecules via hydrogen bonds C-N...HO– Ti.

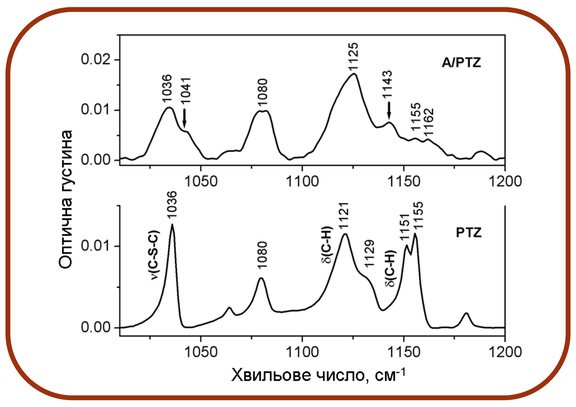
Normalized IR spectra of rutile R1/PTZ and R2/PTZ

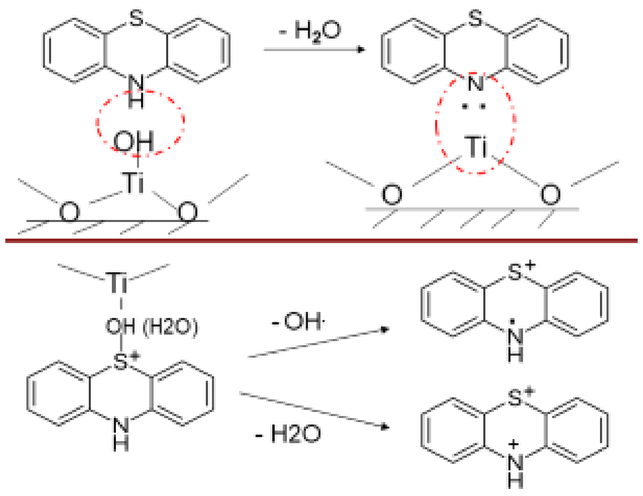




Normalized IR spectra of anatase A-TiO_2, A/PTZ and PTZ

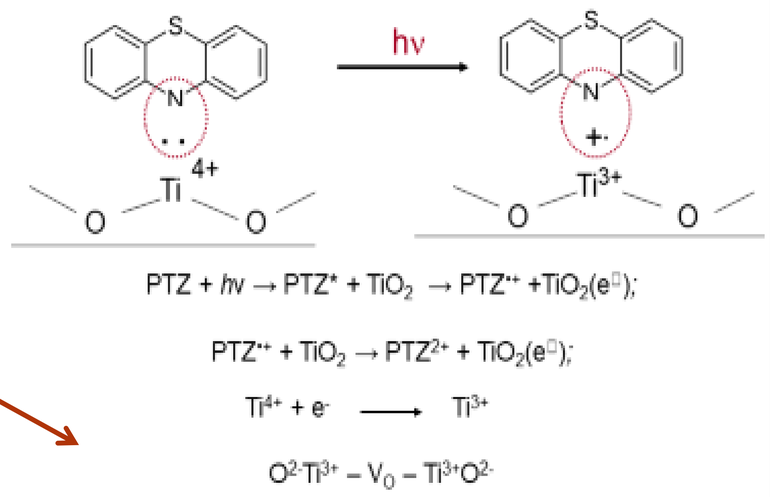






(a)

Schematic representation of the interaction of TiO_2 with PTZ: (a) with the participation of surface OH groups and (b) through the formation of $PTZ^{+\bullet}$ cation-radicals



(b)

Conclusions

For the first time, the interaction of the organic dye phenothiazine with the active centers of the surface of nanosized particles of titanium dioxide of different crystalline modifications is studied on molecular level. It is shown that the interaction of TiO_2 with PTZ occurs with the participation of surface-active Lewis acid centers by charge transfer from PTZ to TiO_2 with the formation of the radical cation $PTZ^{+\bullet}$ and reduced Ti^{3+} ions according to the scheme: $Ti^{4+} + e^- \rightarrow Ti^{3+}$. At the same time, additional oxygen vacancies are created on the TiO_2 surface. The formation of $PTZ^{+\bullet}$ cation-radicals and reduced Ti^{3+} ions causes the color change of the obtained TiO_2/PTZ powders from white to dark blue

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