

# Influence of Manganese Oxides on the Optical Absorption and Photocatalytic Activities of Titanium Dioxide

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**Abstract.** Nanocrystalline titanium–manganese mixed oxides (TMMO) with Mn content of 13–16 at. % were first synthesized by manganese hydroxide precipitation on anatase or rutile particles. UV–vis absorption spectra were investigated in 2.4–6.0 eV region and revealed that compared with pure TiO<sub>2</sub> the presence of manganese oxides results in an increase of the absorption intensity and significant red shift of the TMMO absorption edge. Photocatalytic activity of pure TiO<sub>2</sub>, Mn<sup>2+</sup> doped TiO<sub>2</sub> and TMMO during the photocatalytic decomposition of the safranin dye under UV irradiation was studied. A great improvement of photocatalytic activity is registered for Mn<sup>2+</sup>-doped TiO<sub>2</sub> (anatase and rutile), and rutile-based TMMO sample.

**Key words:** titanium–manganese mixed oxides, optical properties, photocatalysis, safranin dye.

## I. INTRODUCTION

The wide technological usage of TiO<sub>2</sub> for photo-catalysis, is impaired by its large band gap (3 eV for rutile and 3.2 eV for anatase), which requires UV irradiation. In order to improve the photoactivity as well as the response in the visible part of spectrum TiO<sub>2</sub> is doped by different admixtures: ions of transition metals, nitrogen, sulphur, and other [1]. Among them, the couple TiO<sub>2</sub>/MnO<sub>x</sub> seems to present interesting optical and photocatalytic properties.

In the present work the optical and photocatalytic properties of the first synthesized titanium–manganese mixed oxides (TMMO) with different Mn contents (13–16 at.%) were reported.

## II. EXPERIMENTAL

The TMMO samples were synthesized by chemical precipitation of manganese hydroxide on pure polycrystalline TiO<sub>2</sub> particles (rutile or anatase) with subsequent thermal treatment at different temperatures - 300, 850, 900 and 1000°C. According to XRD, EDS, XRF data, the synthesized TMMO materials are polydisperse compounds of different phase composition (Table 1). It is shown that the TMMO-1 anatase sample calcined at 850 °C contain TiO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub> oxides. At the same time, the high-temperature-treated TMMO-2 and TMMO-3 rutile (heated up to 900 and 1000°C) contains also MnTiO<sub>3</sub> in their

structure. The average crystallite sizes of TiO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub> and MnTiO<sub>3</sub> phases in TMMO were determined from XRD line broadening using the Scherrer equation and appeared to be equal to 52-120, 36-45 and 33-40 nm for TMMO, correspondingly. For comparison, the samples of pure rutile and anatase, as well as rutile and anatase surface-doped TiO<sub>2</sub> by Mn<sup>2+</sup> cations by adsorption from MnCl<sub>2</sub> solutions, were synthesized and studied in parallel.

**Table 1. Chemical composition and parameters of the samples**

Sample	T, °C	Mn content, % at.	Phase composition	Phase content, % wt.	Crystallite size, nm ( $D_{hkl}$ )
Pure TiO <sub>2</sub>					
An	300	0	Anatase	100	13.3 (101)
Ru	300	0	Rutile	100	20.8 (110)
Mn <sup>2+</sup> adsorption on TiO <sub>2</sub>					
An/Mn	300	1.0	Anatase	100	15.4 (101)
Ru/Mn	900	1.0	Anatase	10.2	70.8 (101)
			Rutile	89.8	40.3 (110)
Mn hydroxide precipitation on anatase					
TMMO-1	850	13.4	Anatase	54.6	42.2 (101)
			Rutile	35.6	51.7 (110)
			Mn <sub>2</sub> O <sub>3</sub>	9.7	44.8 (222)
Mn hydroxide precipitation on rutile					
TMMO-2	900	15.6	Rutile	85.7	120.8 (110)
			Mn <sub>2</sub> O <sub>3</sub>	12.1	36.0 (222)
			MnTiO <sub>3</sub>	2.2	32.6 (104)
TMMO-3	1000	13.4	Rutile	86.0	62.6 (110)
			MnTiO <sub>3</sub>	14.0	39.9 (104)

The absorption spectra in the UV–vis range for pure TiO<sub>2</sub> (rutile and anatase) and TMMO were measured in 2.5–6.0 eV range. The activity of TMMO and surface-doped TiO<sub>2</sub>/Mn<sup>2+</sup> in the reaction of safranin dye photocatalytic destruction under UV irradiation was studied.

## III. RESULTS AND DISCUSSION

Experimental UV–vis absorption spectra for pure nanocrystalline TiO<sub>2</sub> powder (rutile or anatase) and TMMO samples measured in a photon energy range from 2 to 6 eV are shown in Fig. 1 and Fig. 2. The UV–vis absorption spectra have complicated character, but the main features are invariable for all samples. In the region from 2.5 to 3.0 eV a "tail" absorption of TiO<sub>2</sub>, caused by optical transitions between the states located above the top of the valence band (from 0 to 0.5 eV) and the bottom of the conduction band, are observed. These states can be associated with the bulk structure defects in TiO<sub>2</sub> and can be populated by the thermal excitation of electrons at room temperature from the valence band. It is supposed that a significant increase in the absorption for TMMO-2, 3 rutile by 4-5 times as compared with pure rutile (Fig. 1), is due to the superimposed broad

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absorption bands of  $\text{Mn}_2\text{O}_3$  ( $v_{\text{max}} = 2.5\text{-}2.75$  eV) and  $\text{MnTiO}_3$  ( $v_{\text{max}} = 2.0\text{-}2.5$  eV) in the visible region [2, 3]. For TMMO-rutile the absorption edge is shifted into the visible region of more than 0.5 eV compared to pure rutile.

The intensity of the TMMO-1 anatase absorption is approximately 10 times higher as compared with pure anatase (Fig. 2), and the considerable red shift of the absorption edge is observed.

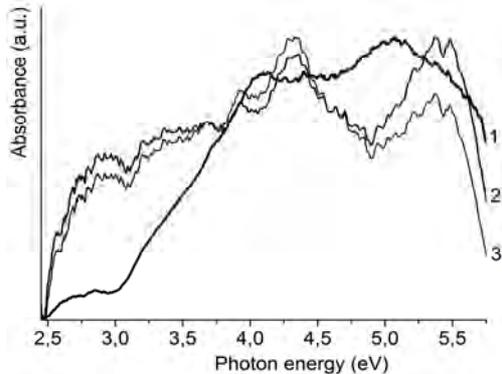


Fig. 1. UV-VIS absorption spectra for rutile: pure (1), TMMO-2 (2) and TMMO-3 (3)

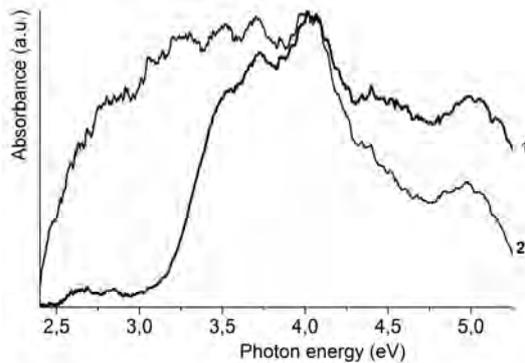


Fig. 2. UV-VIS absorption spectra for anatase: pure (1) and TMMO-1 (2)

It is assumed that in TMMO samples, the presence of manganese oxides results in a creation of additional defect states, which causes an increase of the absorption intensity.

The activity of TMMO and surface-doped  $\text{TiO}_2/\text{Mn}^{2+}$  in the reaction of safranin dye photocatalytic destruction under UV irradiation was studied. A great improvement of photocatalytic activity is registered for  $\text{TiO}_2/\text{Mn}^{2+}$  (anatase and rutile) as well as for rutile-TMMO. The higher photocatalytic activity of Mn-doped  $\text{TiO}_2$  (rutile and anatase) is explained by the presence of  $\text{Mn}^{2+}$  cations on the  $\text{TiO}_2$  surface. The adsorbed  $\text{Mn}^{2+}$  cations are oxidized by VB holes:  $\text{Mn}^{2+} + h^+_{\text{vb}} \rightarrow \text{Mn}^{3+}$ .

The  $\text{Mn}^{3+}$  cations existing on the  $\text{TiO}_2$  surface can act as acceptors or traps for conduction band electrons. So  $\text{Mn}^{3+}$  inhibits electron-hole recombination. Moreover the electrons trapped in  $\text{Mn}^{3+}$  sites can be subsequently transferred to the adsorbed  $\text{O}_2$ , thus also decreasing the electron-hole recombination. When the content of Mn increases, the Mn cations can act as the recombination centers for electron-hole pairs. In addition, the detrimental effect of dopant high concentrations on the photocatalytic reaction rate can be explained by the filter or the reflection effect of the surface species for UV light radiation.

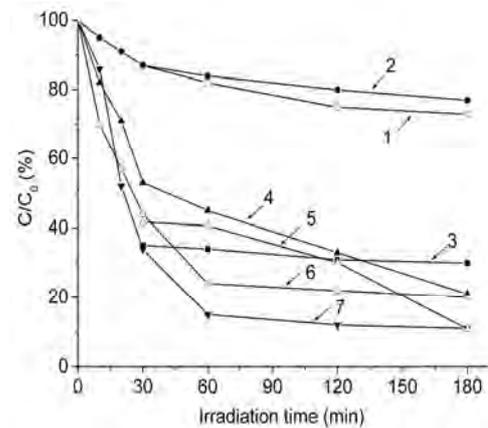


Fig. 3. Photocatalytic degradation of safranin without Ct (1) and with TMMO-1 (2), An (3), TMMO-2 (4), Ru (5), Ru/Mn (6), and An/Mn (7).

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#### IV. CONCLUSIONS

UV-VIS absorption spectra revealed that the presence of  $\text{Mn}_2\text{O}_3$  and  $\text{MnTiO}_3$  results in a significant red shift of the absorption edge for all studied TMMO samples and an increase of the absorption intensity near the absorption edge (2.5-3.0 eV). The disordered structure and the largest number of structure defects together with low UV absorbance at  $\sim 4.9$  eV near the mercury lamp emission maximum can be responsible for the poor photocatalytic activity of the anatase-based TMMO-1. A great improvement of photocatalytic activity is registered for  $\text{Mn}^{2+}$ -doped  $\text{TiO}_2$  (anatase and rutile) as well as for rutile-based TMMO-2 in safranin destruction.

We believe that these  $\text{TiO}_2/\text{Mn}^{2+}$  and TMMO materials can be promising photocatalysts for degradation of organic pollutants under UV and visible light irradiation.

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